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ELEMENTARY QUALITATIVE ANALYSIS

By

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PREFACE

THE historical accidents which have included certain elements in the analytical schemes practised at an elementary stage have also dictated the scope of practically all higher school and intermediate university syllabuses in chemistry. The sooner this departure from chemical realism is remedied, and the consequent disproportionate interest in certain elements adjusted, the better; meanwhile, lack of time compels most students and teachers to confine their attention to this arbitrary selection of material. The descriptive side and the analytical side are, however, usually regarded as separate entities, to be kept severely apart, and very little effort is made to connect the two. The teaching of analysis by rule of thumb has been excused before now on the ground that there was not time to teach all the chemistry that lay behind it. The fact that much of the descriptive work could best be taught by means of analytical reactions, and that the answers to a great many examination questions, of an inorganic as well as of a physical character, are to be found in these reactions, does not seem to have been generally appreciated.

Most text-books appear to ignore the connexion, or even deliberately state that there is none, between the analytical groups and the groups of the Periodic Table. It is not surprising, therefore, to find that few students connect the general character of an element with its analytical reactions. At the same time, it is remarkable how few of them realize why Group I consists, as I have tried to indicate in the text, of such an unsatisfactory assortment as silver, the mercurous ion, and lead. This book is partly concerned with an attempt to show how the reactions used in qualitative analysis depend upon, and are expressive of, the periodic relations of the elements concerned. As an outstanding application of the method one might take the example that, with only one exception, those elements which can be precipitated as sulphides in acid solution occur in nature predominantly as sulphides; those precipitated as hydroxides occur in what might be termed 'mixed oxide' minerals, while those met in the form of carbonate, sulphate, or even phosphate precipitates, occur naturally in those forms. Such a fact is obvious and it has a simple and obvious explanation; yet, so far as I know, it is not usually pointed out. With a very little elaboration it can be seen that the analytical group precipitates summarize most of what the elementary student is expected to know about the sources of the metals he is studying.

The book originated with the last chapter, which was intended to supply that information about procedure and reactions which students frequently need to supplement the tables they are accustomed to use. I have deliberately omitted any such tables, as I am convinced that only those are of real use which the student has had to make up for himself after acquiring the necessary information. The division of the cations into three main groups according to the behaviour of their sulphides is now just over a hundred years old, and was originally due to Liebig. Insistence upon it not only explains the main procedure in analysis, but gives the student a much clearer picture of the process as a whole. The analytical detail is nearly all available in the larger standard works, to which, and to Treadwell and Hall in particular, I here acknowledge my indebtedness. To avoid undue repetition I have summarized some of the principles in the first chapter, and must apologize for the retention of the conception of undissociated salt molecules in order to simplify explanations.

The first and last chapters are therefore the essentials of the book, but the identification of single substances offers such excellent preliminary training in observation and deduction, without too many complications to obscure the main issue, that it was thought advisable to include a section on that part of the work. Finally, for the benefit of those students who have the time and the inclination to acquaint themselves with the reactions which they eventually hope to recognize, I have described the characteristic reactions of the anions and cations, with the appropriate dry tests, making the whole, as far as possible, a comparative study in inorganic chemistry. The reactions in smaller type are such as may conveniently be omitted from a preliminary study.

I have been fortunate in having throughout the generous assistance and kindly criticism of my colleagues, Mr. A. F. Walden, Mr. E. G. J. Hartley, and Dr. B. Lambert, at whose suggestion the book was originally written. The benefit of their experience and knowledge has been invaluable, and while they may have occasionally encouraged me to be unorthodox, they are naturally not to be held responsible for anything which may be found incorrect. I am grateful to my wife for her assistance with proof correction and compilation of the index, and in conclusion I should like to express my thanks to the officials of the Clarendon Press for their unfailing kindness and helpful suggestions while the book was in the press.

F. M. B.

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I

THE THEORETICAL BASIS OF ELEMENTARY QUALITATIVE ANALYSIS

ALL useful chemical research must depend ultimately upon accurate analysis. Analytical processes resolve themselves into two classes; first, *qualitative* tests determining which elements are present in a given substance, and the way in which they are combined with one another; secondly, *quantitative* experiments which determine how much of each component is present. In any branch of physical science quantitative measurements are of the utmost importance, but it is impossible to obtain significant quantitative analyses unless they are controlled by rigid qualitative tests. Furthermore, these tests should be in themselves a guide to quantitative procedure by indicating approximately the relative proportions of the constituents.

It will be obvious that a scheme of analysis which covers all the ninety known elements would be too cumbersome for elementary instruction. A knowledge of the principles available for the separation of elements or groups of elements is more useful. Each new analysis really presents a new set of problems which must be solved by the application of these principles. Chemical history and convention has limited the field of practice, so that the elements and radicals usually dealt with in an elementary treatment of the subject form a somewhat arbitrary selection. They serve very well, however, to typify analytical methods and procedure.

From the point of view of the student analytical work in general and qualitative analysis in particular have further recommendations. In order to differentiate between such a number of elements and their derivatives it is necessary to make use of the majority of typical or characteristic reactions which they undergo. In this way analysis summarizes to some extent the properties of the elements and at the same time illustrates most of the important principles of physical chemistry. Finally it should be kept in mind that as no accurate quantitative result is demanded, there is the greater need for the exercise of personal discretion. In particular this applies to manipulation, and to the recording and interpretation of observations. It is perhaps in this direction that the greatest value can be derived from a course in elementary qualitative analysis.

Electrolytes and non-electrolytes

Substances can be divided into two main groups: those which are decomposed by the passage of an electric current and those whose composition is unaffected thereby. The former are called *electrolytes*, the latter *non-electrolytes*. One important point to be kept in mind in making this distinction is that certain compounds can be electrolytes or non-electrolytes according to circumstance. For example, acetic acid in water is an electrolyte, acetic acid in benzene is a non-electrolyte. Further, it is usually necessary to have a substance in solution or in the fused state before its electrolytic character becomes evident. One part of an electrolyte is found to travel with the current and is therefore positively charged. The residue travels against the current and bears a negative charge. These charged components of an electrolyte were termed by Faraday its *ions*. The positively charged ion travels to the negative electrode (cathode) where it is discharged; it is called the *cation*. The negatively charged ion travels to the positive electrode (anode) and is similarly discharged; it is called the *anion*. The whole process is known as electrolysis and its investigation has furnished the simplest explanation of most of the reactions involved in qualitative analysis.

Electrolytic dissociation

As all the work done by an electric current in electrolysis can be accounted for without utilizing any of it in the actual splitting up of the substance into its ions, it follows that the splitting up must be effected by the medium in which the ions are found. Certain substances acting as solvents are found to be particularly effective in causing the formation of ions, and are known as *dissociating solvents.* When a substance dissolves with formation of ions the process is called *electrolytic dissociation.* By far the most common and the most effective dissociating solvent is water, and the chemistry of aqueous solutions is therefore largely the chemistry of ions. The significance of this in analysis cannot be over-emphasized.

Reactions of ions

When elements or groups of elements exist in solution in the form of ions they can react independently of the other ions with which they were originally associated. Consider the following examples. When a compound of chlorine with a metal (i.e. a chloride) is dissolved in water the chlorine atoms are separated from the metal atoms and each chlorine atom acquires a negative charge. It becomes in fact a chloride ion. It is found that there are a number of reactions common to metallic chlorides in solution, and in each case it is the chloride ion which is responsible for the reaction. For example, silver nitrate solution added to a solution of a metallic chloride gives a white precipitate with definite physical and chemical properties, and this precipitate is the same no matter which chloride is used. In the same way all those silver salts which will upon dissolving dissociate into silver ions and the ions of an acid radical, will give this precipitate when chloride ions are added to their solutions. The acid with which the silver was originally combined does not take part in the precipitation.

Acids, bases, and salts

Before the theory of electrolytic dissociation was formulated the reactions used in qualitative analysis were termed 'reactions of metallic radicals' and 'reactions of acid radicals'. It was well known that there were two kinds of oxide capable of further combination: the acidic group, typified by most of the oxides of the definite non-metals, and the basic group typified by the oxides of the common metals. The acidic oxides gave acids by uniting with water (although acids were known which had no corresponding oxide, e.g. hydrochloric acid). By combination with bases these acids could be made to yield salts, water being formed as the other product of the reaction. In those cases where the acid could react directly with a metal instead of its oxide precisely similar salts were formed, and the metal could be shown to have replaced some or all of the hydrogen in the acid. The acids came to be regarded therefore as salts of hydrogen. The important fact in this connexion which was established by the electrolytic experiments was that in the very great majority of cases the 'salts' of inorganic chemistry were potential electrolytes, and it is now customary to restrict the term *salt* to compounds of this type. Of even greater interest was the fact that hydrogen and the metals (when acting as bases) always formed the positive ion of the electrolyte, whereas the acid radical formed the negative ion. The reason for this has been provided by recent investigations into atomic and molecular structure and can only be indicated briefly here.

The conversion of an element to its oxide and eventually to a salt is known as *oxidation*, and the formation of a metal from its salts or oxides is known as *reduction*. This can also be explained in terms of atomic structure.

Atomic and molecular structure

An atom is made up of a positively charged nucleus neutralized by a group of negatively charged particles or *electrons*. Certain numerical arrangements of these electrons appear to be particularly stable and atoms or groups of atoms will, by means of chemical combination, either surrender or take up electrons if possible in order to establish such favourable arrangements. If it is not possible to effect such an arrangement by transferring electrons from one element to another, then the elements may combine by sharing their electrons. It is now well established that *combination by sharing electrons* results in the formation of non-electrolytes, while *combination by transference of electrons* results in the formation of electrolytes.

Since electrolytes are formed by transference of electrons it is necessary to consider here the effect of that process only. A metal has, as a rule, one or more electrons in excess of a stable arrangement and will, if circumstances permit, get rid of them. As the electrons are negatively charged the metal losing them acquires a positive charge. If it loses one electron, therefore, it becomes a univalent positive ion; if it loses two it becomes a divalent ion, and so on. A non-metal or an acid radical acquiring one electron becomes negatively charged and forms a univalent negative ion. So long as there is equivalence of positive and negative charges, a stable, electrically neutral compound can be formed from ions of the two kinds.

It is also clear that oxidation of a metal corresponds closely to the metal's receiving a positive charge, and reduction to its losing one.

This significance is therefore added to the terms oxidation and reduction, and by an extension of the same idea they came to mean any increase or decrease respectively in the positive valency or charge of an ion as well.

Insoluble substances, and the problem of solution

It may be objected at this point that the majority of compounds known are practically insoluble in water, and it would appear in consequence that analysis dependent upon electrolytic dissociation is necessarily very much limited in scope. Fortunately it is nearly always possible to obtain the ions or potential ions of a substance in solution by means of a few simple devices, but in order that these may be understood it is first necessary to consider the precise meaning of the terms *soluble* and *solubility*.

When a solid and a liquid are allowed to stand in contact with one another a certain amount of the solid will become mixed with the liquid so intimately that the two together form what is called a *homogeneous phase*. This means that any sample of the mixture, or *solution*, taken at random will be indistinguishable in properties from any other sample. For given conditions of temperature and pressure there is always a fixed maximum for the amount of solid which will dissolve in this way in a given quantity of liquid. The solution is then said to be *saturated*, and the percentage of the solid substance present, or more often the number of grams or gram equivalents of 'solid' in a litre of solution, is known as the *solubility* of the solid in the liquid under those conditions. As there is no change in this percentage, once it has been attained, it is clear that any more solid diffusing into the liquid is replaced by an equal amount of solid separating from the solution. This idea is expressed by saying that *the solid is in equilibrium with its saturated solution.*

This equilibrium is similar to the equilibrium established under given conditions between the reactants in a chemical change and the resultants of their action. If the resultants are removed from the sphere of action, the reaction is automatically continued in order to replace them. Precisely, the same thing happens in the solution of solids. If, after dissolving, the molecules of the substance are converted into some other substance, then more of the original solid dissolves in order to replace them. In the light of what has been said about ionization it is clear that the dissolved part of the solid may be in the form of ordinary molecules or in the form of ions. The equilibrium which exists is an equilibrium between the solid and its molecules in solution, but these in turn are in equilibrium with their ions. Although there is at present considerable doubt as to the amount of 'undissociated' salt molecules which can exist in solution, to avoid unnecessary complication it is simplest to assume a definite concentration of these molecules in order to get a satisfactory explanation of many analytical reactions. In the case of a simple salt such as sodium chloride the equilibrium would be represented by the equation:

$$\underset{\text{(solid)}}{\mathrm{NaCl}} \rightleftharpoons \underset{\text{(in solution)}}{\mathrm{NaCl}} \rightleftharpoons \underset{\text{(ions)}}{\mathrm{Na^{\cdot}+Cl'}}.$$

Considering the equilibrium in solution ($\mathrm{NaCl} \rightleftharpoons \mathrm{Na^{\cdot}+Cl'}$) it will be seen that a high value for the solubility of sodium chloride can be attained in two ways. First, if large quantities of sodium ions and chloride ions can exist in solution together, then there need only be a small quantity of undissociated molecules. This is the case with almost all soluble salts. The alternative is that the ions cannot exist together in solution, in which case appreciable solubility can only be due to the presence of the undissociated substance. This state of affairs occurs in many acids and soluble bases, and owing to the small concentration of hydrogen ion which is effective in the case of the acids (or of hydroxyl ion OH′, in the case of the bases) in maintaining the character of the substance in solution, these are known as the weak acids and weak bases.

Solubility product and precipitation

So far it has been assumed that the substances involved have been distinctly soluble in water. Precisely the same explanations are valid for the so-called insoluble substances, only here not only do the constituent ions find it impossible to remain in solution together, but the amount of undissociated material in equilibrium with the solid is often negligibly small. This condition leads to an interesting result. The minute amount of undissociated substance necessary for equilibrium with the solid phase is maintained by the presence of a trace of the solid or a very small concentration of ions. Anything causing recombination of the ions to form more undissociated molecules will ensure the removal of just so many undissociated molecules from the solution.

In a chemical reaction where two substances A and B react to form a substance AB, which can also split up to form A and B again, application of the law of mass action gives the result that, at equilibrium,

$$\frac{\text{concentration of } A \times \text{concentration of } B}{\text{concentration of } AB} = \text{a constant},$$

and this is usually written $\dfrac{[A][B]}{[AB]} = K$, K being called the *equilibrium constant.* If $A^{\cdot}$ and B' are the ions of the salt AB, then the equilibrium constant for ionic dissociation may be written

$$K = \frac{[A^{\cdot}][B']}{[AB]} \text{ or}$$

$$\frac{\text{concentration of cation} \times \text{concentration of anion}}{\text{concentration of undissociated molecules}}.$$

In the case of insoluble substances the concentration of the undissociated molecules in the solutions can be assumed to remain constant for the reason explained above; that is to say, the denominator of the equilibrium constant is itself a constant. The numerator, or the product of the concentrations of the ions, must then also be a constant, and this product is known as the *solubility product* for the ions in question.

Suppose that the sparingly soluble substance AB dissociates as above into the ions $A^{\cdot}$ and B'. Then, if a solution containing $A^{\cdot}$ derived from some soluble salt is mixed with a solution containing B' derived from some other soluble salt, $A^{\cdot}$ and B' will be removed in equivalent quantities as the insoluble salt AB until the equilibrium condition is reached and the product of the concentrations of the two ions is equal to the solubility product for AB. If, for example, a solution of sodium bromide (containing sodium ions and bromide ions) be added to silver nitrate solution (containing silver ions and nitrate ions) then, since the solubility product of silver bromide is very small, silver bromide will separate from the mixed solutions until the necessary low concentrations of silver ion and bromide ion are reached. This is the theoretical explanation of *precipitation.* Such an interchange of ions between two salts is also referred to as *double decomposition*, especially if there is actual separation of two new products.

Common ion effect

The addition of a soluble salt producing one of the ions of a sparingly soluble substance will increase the concentration of that ion. For example, the addition of sodium bromide solution (containing a large concentration of bromide ions) to silver bromide solution causes an increase in the concentration of bromide ion. In order to preserve the solubility product for silver bromide at its constant value the concentration of silver ion must be lowered. This can be effected only by the recombination of some of the silver ions with an equal number of bromide ions, with consequent precipitation of silver bromide, until the concentrations have adjusted themselves to give the true solubility product. The net effect of adding the sodium bromide solution has been to decrease the already small solubility of silver bromide. This is usually referred to as the *common ion effect.*

It is not easy to observe the diminution in solubility of a substance already so insoluble as silver bromide, but a similar effect can be seen with more soluble substances, and in fact often interferes with analytical operations. Concentrated hydrochloric acid added to a concentrated solution of sodium chloride causes a precipitate of sodium chloride crystals as a result of the common ion effect. This reaction is applied to the purification of common salt. A similar precipitate is obtained in the case of barium chloride. The first effect of adding excess of a precipitating reagent will clearly be to ensure more complete precipitation. It will be noticed in practice that this effect is sometimes annulled by the subsequent reaction of the precipitate with the reagent.

Methods of making solutions

In order to obtain a 'solution' of substances insoluble in water it is clearly necessary to reverse the operations which have been discussed above. The substances which are to be added must not provide ions which are already in the substance to be dissolved, but must instead remove at least one of those ions in some form or another. The simplest way of doing this is to rely where possible on the formation of undissociated molecules which are themselves soluble. A typical example is shown in the behaviour of calcium phosphate $Ca_3(PO_4)_2$. This substance is insoluble in water owing to the small solubility product for calcium ions and phosphate ions. Phosphoric acid, however, shows little effective dissociation into hydrogen ions and phosphate ions, that is, the equation $H_3PO_4 \rightleftharpoons 3H^{\cdot} + PO_4'''$ does not proceed very far in a forward direction. The addition of hydrogen ions to an equivalent number of phosphate ions will, on the other hand, remove the majority of them from solution by converting them into *dissolved but undissociated* phosphoric acid. The presence of excess hydrogen ions will repress the dissociation further and remove still more phosphate ions. If the few phosphate ions existing in a saturated solution of calcium phosphate are removed by the addition of hydrogen ions (e.g. by adding hydrochloric acid to the phosphate) more calcium phosphate can go into solution, and the salt will continue to dissolve until the small concentration of phosphate ion in equilibrium with phosphoric acid together with the large concentration of calcium ions now in solution give a value exceeding the solubility product for the salt. It should be remembered that as the ionic equation is $3Ca^{\cdot\cdot} + 2PO_4''' = Ca_3(PO_4)_2$ the solubility product in this case will be $[Ca^{\cdot\cdot}]^3[PO_4''']^2$.

The explanation just given has omitted one characteristic which is an important factor in the chemistry of insoluble salts of weak acids. Many of these acids are *polybasic*; that is to say, they have more than one hydrogen atom replaceable by metals. This means that their dissociation occurs in stages. Taking phosphoric acid again as an instance, its dissociation equilibria are resented by

$$H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4' \rightleftharpoons 2H^{\cdot} + HPO_4'' \rightleftharpoons 3H^{\cdot} + PO_4'''.$$

It forms in consequence a series of salts with sodium, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4, all of which are quite soluble. With calcium the 'acid' salt $Ca(H_2PO_4)_2$ is soluble while the other acid salt $CaHPO_4$ and the normal salt $Ca_3(PO_4)_2$ are practically insoluble. In other words, calcium ions can exist in quantity in solution along with H_2PO_4' ions but not with any considerable amount of HPO_4'' or PO_4''' ions. To effect the solution of the normal phosphate $Ca_3(PO_4)_2$ it will be sufficient to add enough hydrogen ions to form the acid phosphate ion H_2PO_4' by union with the phosphate ions of the salt. It is therefore more correct to say that a solution of calcium phosphate in hydrochloric acid contains calcium ions, chloride ions, and dihydrogen phosphate ions H_2PO_4', together of course with the excess of hydrogen ions, some undissociated phosphoric acid molecules, and minute quantities of phosphate and monohydrogenphosphate ions, PO_4''' and HPO_4''. The relative amounts of these constituents will be governed by an equilibrium more complicated than, but in other respects precisely similar to, those already discussed. Many other examples of insoluble normal salts yielding soluble acid salts will be met with in the course of qualitative analysis.

The method just described is really a special case of a more general method for effecting the solution of an insoluble substance, that is, the removal of one of the ions naturally produced by the substance by the *formation of a more complex ion* which does not cause a precipitate with other ions in the solution. The complex ion will usually dissociate into simpler ions including one or more of the ions of the original substance.

An entirely different method of getting an insoluble substance into solution is to remove one of its ions by a *double decomposition.* It is essential that the products of reaction must include either another insoluble substance, or a substance which can be removed from the reacting system on account of its volatility or ease of decomposition. The solution so obtained is not, of course, a solution containing all the ions of the original insoluble substance. The first type of reaction is used when an insoluble salt is heated with a saturated solution of sodium carbonate. There is a partial decomposition resulting in the formation of the insoluble carbonate of the cation, and a solution containing the anion along with sodium ions and the excess carbonate ions. After filtration the cations may be obtained in solution by treating the residue with dilute hydrochloric acid. This last process is simply an application of the other type of reaction mentioned. The double decomposition of the insoluble carbonate with the acid results in the formation of the feebly ionized, volatile, and easily decomposed carbonic acid H_2CO_3, all three factors helping to displace the equilibrium in favour of a solution containing the ions of the metallic chloride. As an illustration of these methods, the very insoluble substance barium sulphate is partly converted by treatment with sodium carbonate into barium carbonate and sodium sulphate. The sodium sulphate can be removed in aqueous solution by filtration and the residual barium carbonate decomposed by hydrochloric acid to give a solution of barium chloride. Other specific instances of all these methods will be discussed as they arise. In any case, before deciding upon which methods are most suitable for bringing a substance into solution, it is advisable to consider the general scheme of the reactions which are to be carried out with that solution.

The general scheme for the detection of cations

From what has been said about the interaction of chloride ions and silver ions, it will be realized that the simplest way in which an ion can be detected is by its reaction with some other known ion to form an easily recognized insoluble precipitate. To arrange a series of reactions each of which would characterize one ion only is for all practical purposes impossible, although modern methods of micro-chemical analysis, which involve a knowledge of the optical properties as well as the chemical reactions of substances, have gone a long way towards achieving this. An economy of time and effort is made by grouping the ions together according to their reactions with a few typical reagents. Each group is subsequently divided into smaller groups, and ultimately the individual metallic ions are separated from one another. It is often thought that the reactions selected to determine these groups are arbitrary, and chosen merely for the convenient size of the groups which they determine. This idea vitiates any attempt to understand the principles which are being applied *systematically* throughout the whole course of chemical analysis.

Theoretically it should be possible by the application of a single principle, properly controlled, to isolate or detect all the cations in turn. Thus replacement of a metal in solution by the ions of a more electropositive metal (one more ready to form positive ions) or electrolysis of the solution at gradually varying potentials should give this sort of separation. In all these cases in practice complications occur which interfere with the main purpose of the reaction. The principle which is employed in qualitative analysis is similar to those cited, and the modifications which have to be introduced are responsible for the complexity of the analytical separations.

The basic principle of the separation of cations may be summarized as the *variation in the solubility of the metallic sulphides.*

The solubility of metallic sulphides

These compounds may be regarded as salts derived from the acid substance hydrogen sulphide H_2S. This substance has two hydrogen atoms replaceable by metals and therefore has the character of a dibasic acid. It should be able to form two series of salts, and although most solid sulphides are normal salts, in solutions containing hydrogen sulphide there must be equilibrium between the undissociated molecule, its monovalent ion HS', and its divalent ion S''. The equilibrium will be determined by the *dissociation constants* of the reactions

$$H_2S \rightleftharpoons H^{\cdot} + HS' \rightleftharpoons 2H^{\cdot} + S'',$$

and will be parallel in every way to the dissociation of phosphoric acid discussed above. Most of the metallic sulphides are very sparingly soluble in water and therefore have a definite and easily attained solubility product for the concentrations of their ions. In the same way that the amount of silver in solution can be determined by the amount of bromide ion present, so the concentration of a metallic ion which can remain in solution will depend upon the amount of sulphide ion which is added to that solution, if other precipitating anions are absent. *The more soluble the sulphide the greater the concentration of sulphide ion necessary to precipitate it for equivalent concentrations of cations.* As the concentration of sulphide ion is allowed to increase, so the sulphides of the metals should be precipitated in *the order of their increasing solubility.*

It is not easy to regulate the concentration of the sulphide ion directly, but from the dissociation equation it will be seen that the concentration of sulphide ion must diminish as the concentration of hydrogen ion increases, and the regulation of hydrogen ion concentration is a comparatively easy thing. A solution containing a strong acid in moderate concentration will have a high hydrogen ion content which can be gradually reduced by various means. It is instructive at this point to see which metallic sulphides have solubility products so low that they are precipitated even when the hydrogen ion concentration is relatively high.

Before this can be done it is necessary to decide which acid shall be added to increase the hydrogen ion concentration. Two considerations will determine this. First, for convenience, the analyst is limited to the common mineral acids and a few of the simpler organic acids. Secondly, the acid must be a 'strong' acid which will not interfere appreciably with subsequent experiments. If, for instance, the acid were to form insoluble salts with most metals, it would defeat its own purpose by removing the cations from solution before the application of the hydrogen sulphide. Nitric acid is the only common acid which gives a complete series of soluble salts with metals, and it would seem at first sight that this is therefore the obvious acid to use. There is, however, a great objection to the use of nitric acid, and that is its oxidizing action. In addition to acting as an acid and therefore reducing the sulphide ion concentration, nitric acid can oxidize hydrogen sulphide and its salts with formation of sulphur and sulphates, according to the concentration of the acid, and so displace the sulphide equilibrium completely in the wrong direction, besides causing a risk of precipitating insoluble sulphates. Use is actually made of this oxidizing action at a later stage of analysis, and the reactions involved are discussed at that point. For acidifying prior to the use of hydrogen sulphide the choice falls instead upon hydrochloric acid which forms comparatively few insoluble salts, and which is otherwise innocuous.

Precipitation of the sulphides: the First Main Group

In Chapter III are described the reactions of those cations which are (quite arbitrarily) included in most elementary systems of analysis, and substances are there indicated whose solutions will serve as convenient sources of these ions for practising analytical tests. It will be found that the salts of certain cations, e.g. aluminium, arsenic, and the weak bases generally, show an acid reaction in solution without the addition of a free acid. This acid reaction may be disregarded for the present.

The acid reaction is due to *hydrolysis* or interaction of the cation with the hydroxyl ion of water. The ionization equation for water, $H_2O \rightleftharpoons H^{\cdot}+OH'$, gives an equilibrium constant

$$K = [H^{\cdot}][OH']/[H_2O];$$

but since the minute quantity of ions formed in pure water hardly affects the quantity of undissociated water present, the latter may be regarded as constant. The ionic product $[H^{\cdot}][OH']$, therefore, is constant and has been shown by several independent investigations to have a value very near 10^{-14} at ordinary temperatures, that is, the concentration of hydrogen ion or hydroxyl ion in pure water is about 10^{-7} gram equivalents per litre. When a salt of a weak base with a strong acid is dissolved in water it is dissociated into its ions, say $A^{\cdot}$ and B'. If $A^{\cdot}$ is the cation of a weak base it will combine to some extent with the hydroxyl ion in the water to form the undissociated hydroxide, since a weak base is one which is only partially dissociated in water. The anion of the strong acid will not combine appreciably with hydrogen ion, which will therefore be more than equivalent to the hydroxyl ion left in solution. To maintain the ionic product a little more water will dissociate into ions, but as this will produce hydrogen ions and hydroxyl ions in equal quantity there will still be excess of hydrogen ion and the solution will give an acid reaction. Similarly, the salt formed by a strong base and a weak acid, e.g. sodium carbonate, will have an alkaline reaction.

The first step in the main analytical procedure will be the addition of hydrochloric acid to the solution containing the cation. With solutions containing silver, mercurous, or lead ions this causes a precipitate of the metallic chloride to form, and these three ions are therefore removed as chlorides in the course of analysis so that they shall not complicate the precipitation of sulphides by hydrogen sulphide. They are usually referred to as Group I. *Their precipitation should be regarded as incidental to the acidifying of the solution.* Soluble mercurous compounds are rare and lead chloride is incompletely precipitated here, so that the idea often stated or implied that the insoluble chlorides form an analytical group of convenient size is unconvincing.

The main precipitation is now carried out with hydrogen sulphide. By arranging that the hydrogen ion concentration shall be approximately 0·25 *N*, sulphide precipitates will form in solutions containing antimony, arsenic, bismuth, cadmium, copper, mercuric, stannous, and stannic ions. These constitute the group of the *less soluble sulphides* and are usually referred to as Group II. It will be seen later, first, that the constitution of the group is determined to some extent by an arbitrary choice of acid concentration, secondly, that the sulphides of silver and lead are also insoluble in hydrochloric acid of this concentration (there is no mercurous sulphide), and thirdly, that the grouping together of these elements is in keeping with their position in the Periodic Table of the elements (see **Tables I, II,** and **IIA,** pp. 219 and 220). These two groups will be referred to in this book as the *First Main Group.*

Decreasing the hydrogen ion concentration: The Second Main Group

The most natural way of reducing the hydrogen ion concentration of a solution is to dilute the solution, but this can never reduce the concentration below 10^{-7} gram equivalents per litre (the concentration of hydrogen ion in pure water). Such dilution is sometimes used in practice to complete the precipitation of the sulphides of Group II cations. No dilution convenient for analytical purposes would cause more than a partial precipitation of any other sulphides and in most cases it would have no effect at all. Some other device therefore must be adopted for lowering the hydrogen ion concentration and the method used depends upon the small constant ionic product for water which, as explained above, determines that the product of the ionic concentrations of hydrogen ion and hydroxyl ion shall be equal to 10^{-14}. In order to reduce the hydrogen ion concentration it is sufficient to add hydroxyl ions, that is, to neutralize the acid with a base. Of the bases which are easily prepared and normally available in the laboratory the only one which does not itself contain a metallic ion is ammonium hydroxide. As the presence of ammonia or ammonium hydroxide in the original substance is easily determined apart from the main analysis, it is immaterial if more is added, and so this base furnishes a convenient source of hydroxyl ions.

If ammonium hydroxide is added to solutions containing the cations which are not precipitated as sulphides in 0·25 N acid, precipitates of metallic hydroxides are formed in most cases, but not by calcium, strontium, barium, sodium, or potassium ions. In the case of magnesium the precipitation is never complete and some of the other precipitates redissolve in excess of the ammonium hydroxide solution owing to the formation of complex cations. These complications are undesirable as *the aim of adding the ammonium hydroxide is not to precipitate metallic hydroxides but to remove hydrogen ions.* Now these hydroxides, like the sulphides, are precipitated in the order of their solubility products and for a given concentration of cation there will be a definite hydroxyl ion concentration which will cause precipitation. The ideal condition would be attained when sufficient hydroxyl ions had been added to the solution to remove the hydrogen ions, but not enough added to precipitate any of the hydroxides. This is nearly, but not quite, possible in practice, by a further application of the dissociation theory. Ammonium hydroxide is a weak base partially dissociating according to the equation $NH_4OH \rightleftharpoons NH_4^{\cdot} + OH'$. To reduce the concentration of OH' at equilibrium it is necessary to increase the concentration of $NH_4^{\cdot}$ and this can be done by adding an ammonium salt. Since chloride ions are already present at this stage of the analysis, the salt usually added is ammonium chloride. In the absence of a strong base, the concentration of hydroxyl ion in a solution containing ammonium hydroxide and any appreciable quantity of ammonium chloride is so low that only the most insoluble hydroxides are precipitated. At the same time it enables the dissociation of hydrogen sulphide to proceed considerably further than in even a feebly acid solution.

The very insoluble hydroxides which are precipitated under these conditions are those of the aluminium, chromic, and ferric ions. The precipitation of these hydroxides must be regarded as *incidental to the sulphide precipitation* and parallel to the separation of silver, mercurous, and lead chlorides in Group I. The hydroxides may be separated as a distinct group, or, more logically, submitted to the subsequent action of hydrogen sulphide. The precipitates of aluminium and chromic hydroxides are unaffected, as the sulphides of these cations are hydrolysed by water with separation of the hydroxides. The precipitate of ferric hydroxide is converted to ferric sulphide which is still more insoluble than the hydroxide. In addition the sulphides of zinc, manganese, nickel, and cobalt are precipitated. This procedure determines the constitution of an analytical group referred to variously as Group III, Groups IIIA and IIIB, or Groups III and IV, or by the names of characteristic cations. It will be referred to in this book as the *Second Main Group*. For the position of these cations in the Periodic Table see **Tables II, III,** and **IIIA,** pp. 219–221.

The Third Main Group

The sulphides of magnesium, calcium, strontium, and barium are practically insoluble as such, but are split up by water to form comparatively soluble ‘acid salts’ (hydrosulphides, e.g. $Ca(HS)_2$) and hydroxides. These cations, together with sodium, potassium, and ammonium, whose sulphides are both soluble and hydrolysed, constitute the remaining analytical group (Groups IV and V, or sometimes V and VI) which will be referred to in this book as the *Third Main Group*. It will be noticed that these cations belong to Groups IA and IIA of the Periodic Table as indicated by **Table III**, p. 220. The separation of the individual members of these groups will be discussed in Chapter V.

General scheme for the detection of anions

To devise a parallel scheme for the separation of anions would require a soluble weak base forming salts with a large range of solubility, and a simple method of varying the concentration of the cation in solution. It has not yet been found possible to devise such a scheme, as the requisite base does not exist. In practice two courses are open. For reactions in solution a series of cations are chosen, and the anions grouped according to the precipitates which they form with these cations. It is best to make use of at least one cation from each of the three main groups of cations discussed above. Thus the solubility in water and in dilute nitric acid of its barium, nickel, and silver salts helps considerably in the identification of an anion. The behaviour and appearance of the calcium and ferric salts give important auxiliary information.

A simpler method, particularly in dealing with single substances, is to disregard ionic reactions except as confirmatory tests and to liberate the acid molecule corresponding to the anion. This, or its decomposition products, can usually be recognized by some specific test. Naturally there is little 'system' in this process, but two points should be remembered in applying it. First, a weak acid will be set free in the presence of excess hydrogen ion, that is, by the addition of a dilute strong acid to one of its salts. If the weak acid is very volatile (e.g. hydrocyanic acid HCN) or unstable (e.g. carbonic acid H_2CO_3) it will be removed from the reacting system, and the reaction will go to completion in consequence. Dilute hydrochloric acid or dilute sulphuric acid acting on the solid substance will therefore serve to identify the anions of volatile or unstable weak acids, notably carbonate, cyanide, cyanate, nitrite, sulphide, sulphite, thiosulphate, and hypochlorite ions.

Secondly, strong or weak acids, provided that they are moderately volatile or unstable, can be displaced by evaporation of their salts with a relatively non-volatile acid: e.g. $H_2SO_4+2MA = 2HA+M_2SO_4$. *Such a displacement is no indication of the relative strengths (in the ionic sense) of the acids concerned, as equilibrium conditions are upset by the volatility of one of the products.* Concentrated sulphuric acid, heated if necessary, will therefore liberate gaseous products from all salts except those of the stable non-volatile acids, of which the most important are sulphates, phosphates, borates, silicates, and chromates. If there is no visible reaction with either dilute hydrochloric acid or concentrated sulphuric acid, it is quite easy to apply appropriate tests for the members of this last group of anions. A more detailed discussion of the method of analysis for anions is given in Chapter V.

Dry Tests

The presence of a particular element or radical in a substance can often be shown by tests, usually known as *dry tests*, which do not involve ions in solution, and a judicious use of such tests will expedite most analyses. These tests are referred to in the descriptive account of the common radicals given in Chapters II and III, but for convenience they are summarized on pp. 132–138. For suggestions as to their use see pp. 139 and 162.

The identification of a single substance

Although there is no fundamental difference between the analysis of a simple salt and the separation of a complex mixture into its constituent ions, in practice it is far simpler to approach the subject by the identification of single substances. In order to do this, so far as the cation is concerned, all that is necessary is a series of tests which will distinguish between the individuals of a group. Actual separations will be unnecessary and this simplifies matters considerably. For these distinctive tests any principles may be applied other than those involved in the group separations. Each stage in differentiation must involve a new principle and once these principles have been assimilated and the reasons for the order of their application grasped, most of the sheer memory work associated with analytical tables will disappear. What is involved is a real knowledge of the chemistry of the elements concerned and their compounds, and a brief survey of these is given here for guidance. Every one of the experiments indicated should be carried out so that the results can be recognized and its cause correctly assigned should it occur in the treatment of an unknown substance. Only the more important reactions are employed in identifying single substances, but the student is recommended to make himself familiar with the remainder by varying the confirmatory tests which he uses. When he is able to identify a single substance with ease, he should make a careful study of the technique of the group separations. The amount of new information required is relatively little, but successful analysis can result only from a clear understanding of the significance of every step taken.

II

THE ANALYTICAL CHEMISTRY OF THE COMMON ANIONS

The Structure of Anions

A *simple anion* consists of a single atom which has received one or more electrons.

A *complex anion* consists of a group of atoms which have received one or more electrons. The atoms in the group are held together by non-ionized links made up of pairs of electrons. A pair may be formed by each atom concerned contributing an electron. This is called *sharing* and the link is called a simple *co-valent* link, written —. Or it may be formed by one atom contributing both electrons, which it is said to *donate* and the other atom to *accept*, and the link is called a *co-ordinate* link, written →. The characters of the two links are similar in spite of the different mechanism of formation. Atoms or radicals are very often grouped around a central atom in fours or sixes, and it is customary to assume that the central atom receives electrons from the cation initially and then shares or donates, as the case may be, to complete stable electron groups for all the atoms concerned.

Typical anions are:

Simple. F', Cl', Br', I', S''.

The halogens have seven valency electrons and receive one, sulphur has six and receives two.

Complex. (i) By simple sharing.

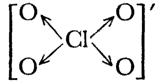
$(H{-}S)'$. Sulphur has six valency electrons, shares one of these with the hydrogen and therefore shares also the single electron which belonged to the hydrogen, and receives its eighth electron from the cation.

$(HgI_4)''$. The mercury atom has two valency electrons, receives two from the cation(s) and each iodine atom contributes one to make four shared pairs in all.

$[Fe(CN)_6]''''$ the ferrocyanide ion. Iron in the ferrous condition makes use of two valency electrons, receives also in this case four from the cations and so can make six shared pairs with the monovalent cyanide radicals. As iron in the ferric condition makes use of three valency electrons, it only requires three from cations to share with six cyanide radicals. Hence the ferricyanide ion is trivalent: $[Fe(CN)_6]'''$.

(ii) By co-ordination.

Typical ions are $(ClO_4)'$, $(SO_4)''$, $(PO_4)'''$, $(SiO_4)''''$,

written  &c.

The chlorine, sulphur, phosphorus, and silicon by receiving one, two, three, and four electrons respectively from the cations make up groups of eight which are donated as four pairs to the oxygen atoms. Each oxygen atom then has six valency electrons plus an accepted pair. An interesting case is the phosphite ion which is dibasic; sodium phosphite is $Na_2(HPO_3)$ and *not* Na_3PO_3. The phosphorus has five available electrons, shares one with the hydrogen in the complex, receives two from the cations, and is thus able to donate three pairs to the oxygen atoms.

For a fuller treatment of the subject see Sidgwick, *The Electronic Theory of Valency*, Oxford, 1927.

Identification of gases

Many tests employed in qualitative analysis, particularly in connexion with anions, depend upon the identification of gases and vapours. A knowledge of the chemistry of these gases should have been acquired before analysis is attempted, but a summary of their more important characteristics is given below. They are classified according to the groups of the Periodic Table and it will be seen that they are mainly elements or oxides or hydrides of elements in the *non-metal* region of the Table. The anions or other substances with which they are normally associated are also given.

HYDROGEN H_2. A colourless gas almost insoluble in water, very much lighter than air, burning with a blue flame to form water, and exploding when mixed with air and ignited. Associated with the *action of dilute acids on metals.*

HALOGENS AND HALOGEN COMPOUNDS

CHLORINE Cl_2. A yellowish-green gas, heavier than air, and moderately soluble in water, with a choking smell and a vigorous bleaching action on *moist* red litmus paper. It will liberate iodine from potassium iodide and hence turn 'starch-iodide' paper blue. Associated with *oxidation of chlorides.*

BROMINE VAPOUR Br_2. A very heavy, orange-red vapour which can be condensed to a red liquid. It has a very unpleasant odour and affects the eyes readily. It should not be confused with the much less dense and sweeter-smelling nitrogen peroxide. Associated with *oxidation of bromides* and with *bromates.*

IODINE VAPOUR I_2. An unmistakable heavy vapour of a deep bright purple colour. Associated with *oxidation of iodides.*

HYDROGEN CHLORIDE HCl. A colourless gas, heavier than air, which dissolves very readily in water to give an acid solution. It fumes in moist air and the fumes produce a sharp irritation in the nose. Its solution gives ionic reactions characteristic of *chlorides* (q.v.), with which it should be associated.

HYDROGEN BROMIDE, HBr, and HYDROGEN IODIDE, HI, are very similar to hydrogen chloride. The three gases are distinguished by their oxidation products, the corresponding free halogens. HBr and HI are associated with *bromides* and *iodides* respectively.

HYDROGEN FLUORIDE H_2F_2. Similar to the other hydrogen halides but with the additional property of etching glass. It cannot be oxidized chemically. Associated with *fluorides* and *silicofluorides*. (See also SILICON TETRAFLUORIDE below.)

CHLORINE PEROXIDE ClO_2. A *very explosive* gas rather more green in colour than chlorine and with a less irritating but pungent smell and vigorous bleaching action. Associated with *chlorates*. *Euchlorine*, a mixture of chlorine and chlorine peroxide which is not explosive, is given off when chlorates are warmed with moderately concentrated hydrochloric acid.

OXYGEN AND SIXTH GROUP COMPOUNDS

OXYGEN O_2. A colourless gas almost insoluble in water which can rekindle a glowing splint of wood. (The only other gas with this property is *nitrous oxide* which is formed in very few reactions, and is less active than oxygen.) Oxygen is associated mainly with *oxides*, *peroxides*, *peracids and their salts*, *chlorates*, *bromates*, *iodates*, and *nitrates*.

OZONE O_3. A colourless gas with a peculiar smell and the power to liberate iodine from potassium iodide. Associated with *persulphates*.

WATER VAPOUR OR STEAM, H_2O, is usually recognized by its condensation to a mist, eventually forming colourless drops of water which give anhydrous copper sulphate the bright blue colour of the pentahydrate. Associated with *hydrated salts* and the *decomposition of organic compounds*.

HYDROGEN SULPHIDE H_2S. A colourless gas, not much heavier than air, with a rather sickly smell noticeable in bad eggs. It is fairly soluble in water and the solution is faintly acid. The gas burns with a steady blue flame forming sulphur dioxide and water, sulphur being deposited if the supply of oxygen is limited.

$$2H_2S+O_2 = 2H_2O+S_2$$
$$2H_2S+3O_2 = 2H_2O+2SO_2.$$

A solution of the gas gives the characteristic reactions of sulphides (q.v.): it reduces potassium permanganate solution (which it decolorizes) and potassium dichromate solution (which is turned green) with the separation of sulphur in each case. It also turns alkaline sodium nitroprusside solution purple, and gives a black precipitate of lead sulphide with an alkaline solution of lead hydroxide (sodium plumbite). Associated with *sulphides.*

SULPHUR DIOXIDE SO_2. A heavy, colourless gas with a choking smell (noticed when sulphur is burnt), very soluble in water. The solution, sulphurous acid, has a slow bleaching action on moist red litmus paper and a rapid reducing action on potassium permanganate solution (which it decolorizes) and on potassium dichromate solution (which it changes from orange to green). A paper soaked in potassium dichromate solution usually looks greenish-yellow; it is better to use a drop of the solution on a glass rod suspended in the gas for this test. Associated with *sulphites* and *thiosulphates,* and the action of *reducing agents on concentrated sulphuric acid.*

CHROMYL CHLORIDE VAPOUR CrO_2Cl_2. This is a red vapour similar in appearance to bromine but less volatile. It is formed by the action of sulphuric acid on a mixture of a *chloride* and a *chromate.* There is a similar compound *chromyl fluoride* but no corresponding compounds of bromine or iodine.

NITROGEN AND FIFTH GROUP COMPOUNDS

NITROGEN N_2. A colourless insoluble gas with no simple reactions giving 'positive' results. It neither burns nor supports combustion nor can it show any characteristic reactions in solution. Associated with the *oxidation of ammonia and decomposition of some of its compounds,* e.g. ammonium nitrite, dichromate, and persulphate.

AMMONIA NH_3. A colourless gas, lighter than air, with a pungent odour, which does not burn in air or support combustion. It is extremely soluble in water and is the only common gas or vapour giving an alkaline reaction in solution. Turmeric paper which is turned brown by the gas is probably more sensitive as a test than red litmus paper. It gives a brown precipitate with *Nessler's Reagent* (a solution of mercuric iodide in potassium iodide made alkaline with potassium hydroxide). Associated with *ammonium compounds* and the *reduction of nitrogen compounds* in general.

PHOSPHINE, PH_3, and ARSINE, AsH_3, are very poisonous gases with unpleasant odours, readily combustible and giving black precipitates with silver nitrate. Phosphine is associated with *phosphides, hypophosphites* and *phosphites*; arsine with the *reduction of arsenic compounds by nascent hydrogen.*

NITROUS OXIDE N_2O. A colourless gas, heavier than air, with a very faint sweet smell, somewhat soluble in water the solution being neutral to litmus. The gas can rekindle a brightly glowing splint. Associated with *ammonium nitrate* and the *action of dilute nitric acid on zinc.*

NITRIC OXIDE NO. A colourless gas which unites immediately with the oxygen of the air to form brown fumes of nitrogen peroxide. It does not burn but supports the combustion of things already burning well. It forms a dark brown compound with ferrous sulphate. Associated with *nitrites* and the *reduction of dilute nitric acid* by metals and otherwise.

NITROGEN PEROXIDE NO_2 (N_2O_4). A heavy, brown gas with a rather sweet but choking smell, giving a colourless acid solution in water in which it is very readily soluble. The solution gives the reactions of nitrous and nitric acids (q.v.). Associated with *nitrites, nitrates, and concentrated nitric acid.*

FOURTH GROUP COMPOUNDS

CARBON MONOXIDE CO. A colourless gas, insoluble in water, which burns with a blue flame to form carbon dioxide. (To ignite the gas place the mouth of the test-tube from which it is issuing just below the bottom of the Bunsen flame.) It is soluble in an ammoniacal solution of cuprous chloride. Associated with *cyanides*, *complex cyanides*, *formates*, *oxalates*, and *tartrates*.

CARBON DIOXIDE CO_2. A colourless gas, heavier than air, which neither burns nor supports combustion. It is moderately soluble in water, the solution (carbonic acid) being weakly acidic and showing reactions of soluble carbonates (q.v.), e.g. a white precipitate of calcium carbonate with calcium hydroxide ('turning lime water milky'). Excess CO_2 redissolves this to form the soluble calcium bicarbonate. Associated with *carbonates*, *cyanates*, *oxalates*, and *tartrates*.

METHANE CH_4. A light, colourless gas which burns with a non-luminous flame to give carbon dioxide and water. It is insoluble in water and is *not* absorbed by ammoniacal cuprous chloride solution.

ETHYLENE C_2H_4. A colourless gas burning with a slightly smoky flame to give carbon dioxide and water. It is insoluble in water but decolorizes bromine water owing to the formation of ethylene dibromide, $C_2H_4Br_2$.

ACETYLENE C_2H_2. A colourless gas with an unpleasant penetrating odour which burns to carbon dioxide and water, decolorizes bromine water and gives a black precipitate with silver nitrate solution.

These three hydrocarbons are associated with various *carbides*.

SILICON TETRAFLUORIDE SiF_4. A colourless gas readily hydrolysed to hydrofluoric and fluosilicic acids, usually with separation of silica. Associated with *silicates* and *fluosilicates*.

Characteristic reactions of the anions and their solid salts

The reactions of the common anions constitute a large part of the chemistry of the non-metallic elements. In addition certain metals form important anions as well. In the following summary of reactions of acid radicals the ionic reactions described are mainly those in which characteristic precipitates are formed with the identifying cations: calcium, barium, nickel, iron, and silver. The solutions which should be used for these tests are: calcium nitrate (or chloride), barium nitrate (or chloride), nickel nitrate, ferric chloride, silver nitrate. The reactions of the solid salts with dilute hydrochloric acid and concentrated sulphuric acid are given for each anion. The theory of these reactions is outlined on pp. 21 and 22. A few special reactions useful for rapid identification or confirmation are also included. The tests for each anion should be carried out by the student, using the sodium or potassium salt unless some other salt is indicated. Equations of reactions which are 'double decompositions' are usually omitted.

The Halogen Acids

I. Fluorides, chlorides, bromides, iodides

The compounds HYDROGEN CHLORIDE HCl, HYDROGEN BROMIDE HBr, and HYDROGEN IODIDE HI are colourless gases. HYDROGEN FLUORIDE HF is a volatile liquid boiling at 19° C. The aqueous solutions of these compounds constitute hydrochloric, hydrobromic, hydriodic, and hydrofluoric acids respectively, giving rise to chlorides, bromides, iodides, and fluorides. The normal salts are not appreciably decomposed by heat.

COLOUR AND SOLUBILITY OF SALTS

Most chlorides are soluble in cold water, the insoluble chlorides forming the first group precipitate in the analysis for cations (**Table I**, p. 219). These are *silver chloride* AgCl, *mercurous chloride* Hg_2Cl_2, and *lead chloride* $PbCl_2$, the last being sparingly soluble in cold water and readily soluble in boiling water. *Cuprous chloride* is also insoluble in water. The chlorides of colourless cations are themselves colourless.

The bromides are in almost all cases similar to the chlorides in solubility and colour (silver bromide is, however, creamy yellow rather than colourless, and anhydrous cupric chloride is brownish-yellow while the bromide is definitely brown).

The iodides of the heavy metals show marked differences from the chlorides and bromides.

(*a*) *Colour.* The following *solid* iodides are coloured: silver (yellow), mercurous (grey-green), mercuric (red and yellow), stannous (orange), stannic (red), lead (golden yellow), arsenic (red), antimony (red: oxyiodide yellow), bismuth (black). The corresponding chlorides and bromides are colourless.

(*b*) *Solubility.* Of the above iodides, the *silver*, *mercurous*, *mercuric*, *lead*, *stannous*, and *bismuth* salts are insoluble in cold water. The rest are slowly hydrolysed by it. Lead iodide gives a colourless solution in hot water. *Cuprous iodide* (white) is also insoluble in water.

Note that cupric, chromic, and ferric iodides are unknown.

(*c*) *Complex ions.* Iodides often dissolve in potassium iodide solution forming complex anions which are usually colourless:

$$HgI_2+2KI = K_2(HgI_4).$$

The alkali iodides unite with iodine (and in some cases with the other halogens) to form polyhalides:

$$KI+I_2 = KI_3.$$

It will be seen from the above remarks on iodides that potassium iodide is a very valuable reagent in confirmatory tests for cations.

Fluorides also differ in solubility, but not as a rule in colour, from chlorides and bromides. *The fluorides as a class are insoluble in water,* but the *fluorides of potassium, sodium, ammonium, silver, and mercury are soluble.* Double or complex fluorides are readily formed, cf. cryolite Na_3AlF_6 ($\equiv 3NaF+AlF_3$), but these are not as a rule as soluble as the complex iodides.

ACID AND BASIC SALTS

The only acid salts of importance in this group are the acid fluorides (e.g. KHF_2) which exist because the acid acts in many ways as if it were H_2F_2 rather than HF. Two basic compounds are important: the oxychlorides of antimony and bismuth (SbOCl or $Sb(OH)_2Cl$ and BiOCl) which are insoluble and are precipitated when solutions of the corresponding chlorides ($SbCl_3$, $BiCl_3$) are considerably diluted.

Identification

With the dry salts.

1. Dilute hydrochloric acid gives no reaction.

2. Concentrated sulphuric acid liberates from a

fluoride: hydrogen fluoride HF, a colourless acid gas with the power to etch glass.

chloride: hydrogen chloride HCl, a colourless acid gas.

bromide: hydrogen bromide HBr (similar to HCl), and at the same time oxidizes part of it to bromine, which is given off as a red-brown vapour.

$$H_2SO_4+2HBr = Br_2+SO_2+2H_2O.$$

iodide: hydrogen iodide HI (similar to HCl and HBr) and simultaneously iodine by oxidation. This separates as a black solid readily volatilizing to a violet vapour.

These reactions usually take place readily in the cold. Sometimes a little heating is necessary, especially with fluorides. It is difficult to get the free acids from the chlorides, bromides, and iodides of mercury (-ous), lead, and tin (-ous).

3. If the salt be mixed into a paste with an equal quantity of manganese dioxide and a little water, and treated with concentrated sulphuric acid the *free halogen* is liberated with chlorides, bromides, and iodides, but not with fluorides. (Fluorine attacks water so readily that it is impossible to oxidize hydrogen fluoride to fluorine in the presence of water.)

In the case of the salts mentioned in **2** above which do not give the free acid readily, potassium permanganate should be used instead of manganese dioxide.

Chlorine is a gas which may be recognized by its greenish-yellow colour, its smell, and its rapid bleaching action on moist red litmus.

Bromine is a dense deep-red liquid with an orange vapour.

Iodine is a dark purple solid with a violet vapour, which turns starch blue.

4. If potassium dichromate be substituted for manganese dioxide in test **3** above, there is formed in the case of chlorides a volatile red liquid, *chromyl chloride* CrO_2Cl_2, in addition to some chlorine. This substance is hydrolysed in solution to chromic and hydrochloric acids. A similar compound chromyl fluoride exists, but no such compound is formed by either bromides or iodides in these circumstances.

$$K_2Cr_2O_7+3H_2SO_4+4KCl = 2CrO_2Cl_2+3K_2SO_4+3H_2O.$$

5. If a fluoride is mixed with finely divided silica in a metal crucible and a drop of concentrated sulphuric acid placed on the mixture, *silicon tetrafluoride* SiF_4 is evolved. By placing a watch glass carrying a drop of water on its under (convex) surface over the crucible, a 'skin' of silica is formed on the drop by hydrolysis of the silicon tetrafluoride. (The watch glass must not be left long enough for the hydrogen fluoride given off to attack the glass.)

With solutions.

6. Barium, calcium, nickel, and ferric ions cause no precipitate with chloride, bromide, or iodide ions (though ferric compounds can liberate iodine by oxidation of iodides), but with a neutral solution of a *fluoride*

(*a*) barium nitrate gives a white precipitate of barium fluoride which is very sparingly soluble in dilute nitric acid;

(*b*) calcium nitrate gives a white precipitate of calcium fluoride insoluble in acetic acid, but soluble in dilute hydrochloric acid.

7. Silver nitrate gives no precipitate with a neutral solution of a fluoride (silver fluoride being very soluble in water). With chlorides, bromides, and iodides in solution silver nitrate gives characteristic precipitates insoluble in dilute nitric acid. These are:

(*a*) *Silver chloride* AgCl; colourless, curdy, and turning purple-grey on exposure to sunlight. Soluble in ammonium hydroxide solution (cf. **Silver 7**, p. 84):

$$AgCl + 2NH_3 = [Ag(NH_3)_2]Cl.$$

(*b*) *Silver bromide* AgBr; cream-yellow, otherwise similar to the chloride except that it is much less soluble in ammonium hydroxide solution (a comparatively large volume of hot ammonium hydroxide is necessary).

(*c*) *Silver iodide* AgI; a yellow precipitate which is insoluble in ammonium hydroxide solution.

The anions of these insoluble silver salts are easily brought into solution by displacement of the silver with metallic zinc. The halide is suspended in dilute sulphuric acid and granulated zinc added. There is sufficient silver ion present for silver to be deposited and zinc to go into solution. More halide then dissolves and all is eventually converted to metallic silver and a solution of zinc halide which can be decanted or filtered.

8. A halogen can as a rule displace a halogen of higher atomic number from its binary compounds; e.g. chlorine water added to a solution of a bromide liberates *bromine*, which gives a red colour to the solution, and which can be extracted by adding a few drops of carbon disulphide. The solution of bromine in carbon disulphide is orange-brown. With a solution of an iodide chlorine water liberates *iodine* which dissolves in the excess iodide to give a brown solution. Extraction with carbon disulphide gives a violet coloured solution of iodine (compare the colour of iodine vapour). Excess chlorine oxidizes the iodine in the aqueous layer to iodate ion which is colourless. The partition equilibrium is disturbed and the violet colour consequently disappears.

II. Oxyacids of the Halogens

No oxyacids of fluorine have as yet been identified. Chlorine forms HYPOCHLOROUS ACID $HClO$, the hypothetical chlorous acid $HClO_2$ of the chlorites, CHLORIC ACID $HClO_3$, and PERCHLORIC ACID $HClO_4$. Bromine forms HYPOBROMOUS and BROMIC acids. Iodine forms HYPOIODOUS, IODIC, and several PERIODIC acids.

Of the salts of these acids the hypochlorites, chlorates, bromates, iodates, and perchlorates are the most important.

Hypochlorites

Hypochlorous acid $HClO$ is known only in aqueous solution. The sodium and potassium salts of this acid are formed along with the corresponding chlorides when chlorine is passed into *cold* solutions of the hydroxides of these metals.

$$2KOH+Cl_2 = KClO+KCl+H_2O.$$

'Bleaching powder', the product of the action of chlorine on slaked lime, is not a pure compound, but consists principally of calcium united to one chloride and one hypochlorite radical. It behaves in solution therefore, owing to the dissociation of these radicals, as a mixture of chloride and hypochlorite.

The free acid can be prepared in solution by passing chlorine into a suspension of yellow mercuric oxide.

$$2Cl_2+2HgO+H_2O = 2HClO+Hg_2OCl_2.$$

The solution is unstable, especially in presence of light, and decomposes, giving hydrochloric acid and oxygen. The hydrochloric acid so formed will react with more hypochlorous acid to give chlorine (see below) the smell of which usually accompanies all hypochlorites.

Hypochlorites decompose in solution especially on heating, forming a mixture of chlorates and chlorides. Hence these are the products of chlorine on hot alkaline hydroxide solutions. The ion ClO' is colourless.

SOLUBILITY. The hypochlorites which are known are all soluble in water, and are hydrolysed, giving alkaline solutions.

Identification

With the dry salts.

1. The most characteristic reaction of hypochlorites is their decomposition by cold dilute hydrochloric acid. Chlorine is given off and chlorides are left in solution.

$$NaOCl+2HCl = Cl_2+NaCl+H_2O.$$

This is really the reverse of the action of cold water (or alkali) on chlorine.

With solutions.

Ionic reactions of hypochlorites in solution are vitiated by the presence of chloride ion which is almost invariably present, but the solutions give characteristic *oxidizing reactions* owing to the readiness with which oxygen is removed from the anion.

2. The addition of a hypochlorite in alkaline solution to a soluble lead salt (nitrate or acetate) gives a chocolate-coloured precipitate of lead dioxide.

$$2NaOH+NaOCl+Pb(NO_3)_2 = NaCl+2NaNO_3+PbO_2+H_2O.$$

3. A drop of cobalt nitrate solution added to a solution of a hypochlorite gives a black precipitate of cobaltic oxide Co_2O_3. On warming, the solution evolves oxygen (which will rekindle a glowing splint). This decomposition of hypochlorites to give oxygen appears to be catalysed by the Co_2O_3 formed.

Hypobromites and hypoidites exist in solution but are comparatively unimportant.

Chlorates, bromates, and iodates

Free chloric and bromic acids can be liberated in solution but the solutions are unstable. Iodic acid is a stable white solid which can be prepared by oxidizing iodine with nitric acid. The ions ClO_3', BrO_3', and IO_3' are stable, monovalent, and colourless.

SOLUBILITY. All chlorates are soluble, but all bromates except those of the alkali metals, magnesium, and calcium are insoluble, while the iodates of the alkali metals only are soluble.

Identification

With the dry salts.

1. Heating the normal salts strongly liberates *oxygen* leaving the corresponding halide, but in the presence of acids the free halogen will be liberated (see **8** below). In the case of chlorates *perchlorates* may be formed as intermediate products of the decomposition

$$4KClO_3 = 3KClO_4 + KCl$$
$$2KClO_3 = 2KCl + 3O_2.$$

2. Cold dilute hydrochloric acid has no reaction with chlorates or iodates, but chlorine and bromine result from its action on bromates. On warming a chlorate with hydrochloric acid *chlorine dioxide* ClO_2, mixed with varying quantities of chlorine according to the strength of the acid used, is evolved. This gas is rather deeper in colour than chlorine and has its own characteristic smell.

3. Concentrated sulphuric acid has no visible effect on iodates, but it reacts violently with chlorates from which it liberates the explosive gas *chlorine dioxide*, and with bromates from which *bromine* mixed with hydrogen bromide is evolved. *These tests must be carried out with very small quantities of material and with great caution.*

With solutions.

4. As all chlorates are soluble they give no characteristic precipitates.

5. With neutral solutions of *bromates* or *iodates* barium nitrate gives a white crystalline precipitate often very slow to form, especially with bromates. The solution should be agitated to start crystallization. The precipitates are soluble with difficulty in dilute nitric acid.

6. Calcium nitrate gives a similar precipitate with *iodates* only; it is practically insoluble in acetic acid.

7. Silver nitrate gives with bromates and iodates white precipitates soluble in dilute nitric acid.

ACTION OF REDUCING AGENTS

8. The action of zinc and dilute sulphuric acid, or of boiling ferrous sulphate solution, or of sulphurous acid is to reduce solutions of chlorates, bromates, or iodates to the corresponding halides.

By the use of an insufficient quantity of reducing agent in acid solution, e.g. sulphurous acid, a further reaction can take place, namely, the liberation of free halogen due to the oxidation of the halide by the residual oxysalt. The liberation of iodine from hydrogen iodide by the action of iodate ions is rapid and complete, the corresponding liberation of bromine is slower, while the oxidation of hydrochloric acid by chlorates in cold dilute solutions is negligible. All three reactions are the reverse of the action of hot water or alkali on halogens. Compare, for example, the equations

$$3Cl_2+3H_2O = 5HCl+HClO_3 \quad (1)$$

$$3Cl_2+6NaOH = 5NaCl+NaClO_3+3H_2O. \quad (2)$$

The presence of alkali displaces the equilibrium of equation (1) to the right, while acid displaces it to the left.

$$HIO_3+5HI = 3I_2+3H_2O.$$

The equilibrium of this reaction, other things being equal, is considerably more in favour of the formation of free halogen than in the case of chlorine.

Perchlorates

These are the most stable salts of the halogen oxyacids and therefore give few 'positive' reactions. Their stability is probably due to the symmetry of the ion $(ClO_4)'$. The ion is colourless. The free anhydrous acid $HClO_4$ is quite stable at ordinary temperatures. It is a colourless liquid boiling, with decomposition, below 100° C. Its solution in water is a strong acid.

SOLUBILITY. The perchlorates are generally soluble, those of the alkali metals being amongst the least soluble.

Identification

With the dry salts.

1. Strong heating liberates oxygen, leaving the chloride as residue (as perchlorates are probably the first decomposition products of chlorates it is obvious that a higher temperature is needed for their decomposition than for that of the corresponding chlorates).

2. In contrast to chlorates neither dilute hydrochloric acid nor concentrated sulphuric acid has any visible reactions with perchlorates.

With solutions.

3. Again in contrast to chlorates, reduction to chloride by means of a ferrous salt, zinc and sulphuric acid, or sulphurous acid is impossible. Titanous sulphate can effect this reduction.

4. As perchlorates are generally soluble they give no precipitation reactions of any value analytically.

Oxides

Since the accepted system for the description of inorganic compounds is mainly based on the formation of oxides and the interaction of these oxides, they can hardly be regarded as salts, although some oxides are electrolytic in character. It is sometimes convenient, however, to regard the oxygen in metallic oxides as an anion and to remember that a 'single substance' may be an oxide when tests for all other anions have failed to give positive results. Confirmation must then depend upon a knowledge of the specific physical character and the reactions of these compounds, and these are indicated briefly with their respective metals (Chap. III).

The following classification of oxides should be noted.

(*a*) ACIDIC. (1) Normal, and some lower, oxides of non-metals; e.g. P_2O_5, SO_3, SO_2. They usually dissolve in water to give solutions of acids, and in alkalis to form salts.

(2) Oxides of some metals in their highest states of valency; e.g. CrO_3. They usually yield oxygen on heating strongly and some are soluble in water yielding acids.

(*b*) BASIC. (1) Normal oxides of the metals, soluble in acids to form salts; e.g. NiO, MgO.

(2) Peroxides, derived from *hydrogen peroxide*, and yielding this substance on treatment with dilute acids; e.g. BaO_2.

(3) 'Polyoxides'; oxides of metals in an abnormally high state of valency, other than acidic oxides (2); e.g. PbO_2, MnO_2. They yield *oxygen* on treatment with sulphuric

acid and *chlorine* on treatment with concentrated hydrochloric acid.

(4) Mixed oxides, yielding compounds of a metal in different states of valency on treatment with acids; e.g. Fe_3O_4, Pb_3O_4.

$$Fe_3O_4+4H_2SO_4 = FeSO_4+Fe_2(SO_4)_3+4H_2O.$$
$$Pb_3O_4+4HNO_3 = 2Pb(NO_3)_2+PbO_2+2H_2O.$$

(*c*) NEUTRAL OXIDES and SUBOXIDES of which the more important are gaseous; e.g. N_2O, CO.

Oxides of metals which form hydroxides soluble in acids or alkalis are sometimes called 'amphoteric' but the adjective is more strictly applied to the hydroxides only; e.g. $Al(OH)_3$, $As(OH)_3$.

Hydroxides

These are either *soluble*, in which case they can be obtained by dissolving the corresponding oxide in water, or *insoluble*, in which case they can be precipitated by the action of a soluble hydroxide on a solution containing the required cation.

All hydroxides except those of the alkali elements and the ammonium radical can be dehydrated more or less completely by heat to give the oxide. It should be noted that acids are hydroxylic in form but not in dissociation.

The Sulphur Acids

Sulphur is a constituent of a great many acids of which more than a dozen contain sulphur, hydrogen, and oxygen only. In addition to these the gas HYDROGEN SULPHIDE H_2S dissolves in water to form a very weak acid. The principal oxyacids of sulphur include SULPHUROUS ACID H_2SO_3, THIOSULPHURIC ACID $H_2S_2O_3$, SULPHURIC ACID H_2SO_4, and PERSULPHURIC ACID $H_2S_2O_8$.

The remainder are 'CARO'S ACID' or permonosulphuric acid H_2SO_5 and the THIONIC acids of general formula $H_2S_nO_6$ ($n = 2$, 3, 4, 5, or 6). Details of the reactions of these acids and their salts must be left to larger text-books.

Sulphides

The acid character of hydrogen sulphide solution and its dissociation have been discussed in Chapter I. The gas itself is described on p. 27. The sulphides are as a rule stable to heat but are oxidized on heating in air to give sulphur dioxide and the oxide of the metal.

Colour and solubility. The sulphide ions and hydrosulphide ion HS′ are colourless, but the *solid* sulphides of the 'heavy metals' have characteristic colours which are of great use in the identification of cations. Thus the sulphides of silver, mercury, lead, copper, iron, nickel, and cobalt are black (mercuric sulphide may be bright red, '*vermilion*'; precipitated copper sulphide looks very dark brown), bismuth sulphide is dark brown, and stannous sulphide light brown; antimony sulphide is orange, arsenic, cadmium and stannic sulphides yellow, and manganese sulphide green or reddish-brown (but flesh-coloured when precipitated). Aluminium sulphide (yellow) and chromium sulphide (grey) are rarely seen in a pure state and are hydrolysed by water. The remaining sulphides considered in this book are colourless. Naturally occurring sulphides vary considerably in colour, e.g. pyrites which is golden. There is no mercurous sulphide.

The solubility of the sulphides is the basis of the cation separation and is discussed in Chapter I. See also **Table II**, p. 219. Most sulphides are insoluble in water, though some are slowly hydrolysed by it. The soluble sulphides (those of the alkali metals) are also hydrolysed, and show therefore an alkaline reaction in solution and smell of hydrogen sulphide when moist.

Identification

With the dry salts (use *zinc sulphide*).

1. Dilute hydrochloric acid decomposes some sulphides, liberating *hydrogen sulphide* which can be identified by its smell and action on solutions of potassium permanganate and potassium dichromate (see **7** and **8** below). Those sulphides which are precipitated in the presence of dilute acid are not readily attacked. Concentrated hydrochloric acid should be used if the sulphide of one of these metals is suspected, or test **3** applied to them.

2. Sulphides reduce concentrated sulphuric acid on warming, sulphur dioxide being evolved and sulphur deposited. The reduction of sulphuric acid is however effected by many other substances.

$$ZnS + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2 + S.$$

3. If an insoluble sulphide is added to hydrochloric acid which contains a piece of tin, the hydrogen generated forms hydrogen sulphide which can be detected by the black stain of lead sulphide which it will cause on a filter paper soaked in sodium plumbite (lead hydroxide dissolved in sodium hydroxide solution). The use of a strongly alkaline solution ensures precipitation with a minimum of sulphide ion.

$$H_2S + Pb(ONa)_2 = PbS + 2NaOH.$$

With solutions (use a solution of *sodium sulphide*).

4. Barium and calcium ions produce no precipitate when added to a neutral solution of a sulphide as the corresponding sulphides are hydrolysed by water to form soluble hydrosulphides and hydroxides.

5. Nickel nitrate solution gives a black precipitate of nickel sulphide when added to a neutral solution containing sulphide ions.

6. Silver nitrate solution gives a black precipitate of silver sulphide insoluble in cold dilute nitric acid but oxidized slowly by hot dilute nitric acid.

7. Hydrogen sulphide or sulphides in solution reduce acidified potassium permanganate solution with liberation of sulphur. The solution is decolorized.

$$5H_2S + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S.$$

8. A similar reduction with liberation of sulphur results from the action of sulphides on potassium dichromate solution. The resulting solution is green.

$$3H_2S+K_2Cr_2O_7+4H_2SO_4 = K_2SO_4+Cr_2(SO_4)_3+7H_2O+3S.$$

9. When added to an alkaline solution of *sodium nitroprusside* $Na_2[Fe(CN)_5NO]2H_2O$, hydrogen sulphide gives an intense violet colour to the solution.

Sulphites

Sulphurous acid H_2SO_3 exists in solution only. It decomposes readily into the gas *sulphur dioxide* SO_2 and water. The reactions of moist sulphur dioxide (see p. 28) are essentially the reactions of sulphurous acid. The sulphites, except those of the alkali metals, are decomposed on strong heating, giving off sulphur dioxide and leaving the oxide of the metal. The sulphite ion is colourless.

SOLUBILITY. The sulphites are nearly all insoluble in water: those of the alkali metals are soluble. Soluble bisulphites of the alkaline earths are known in solution.

Identification

With the dry salts.

1. Dilute hydrochloric acid decomposes sulphites and evolves *sulphur dioxide* SO_2; the gas is given off vigorously on warming and may be recognized by its smell and its action on potassium dichromate solution as described on p. 28 (see **5** below).

Note that as any *reducing agent* may produce sulphur dioxide from *concentrated sulphuric acid*, the formation of this gas by the action of that acid on a dry salt is *not* necessarily an indication that a sulphite is present.

With solutions.

2. (*a*). Barium nitrate solution gives with neutral solutions of sulphites a white precipitate of barium sulphite readily decomposed by acids.

(*b*) Calcium nitrate solution gives a white precipitate of calcium sulphite readily soluble with decomposition in acetic acid.

3. Silver nitrate solution gives a white precipitate of silver sulphite soluble with decomposition in dilute nitric acid.

4. Sulphurous acid or sulphites in acid solution will reduce (and hence decolorize) potassium permanganate solution.

$$5H_2SO_3 + 2KMnO_4 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O.$$

(Note that sulphur dioxide will effect this reduction without the addition of further acid.)

5. Sulphites will similarly reduce an acid solution of potassium dichromate, the colour of the solution changing from orange to green.

$$3H_2SO_3 + H_2SO_4 + K_2Cr_2O_7 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O.$$

Thiosulphates

Thiosulphuric acid $H_2S_2O_3$ is unstable and decomposes upon formation into sulphur dioxide, sulphur, and water. The sulphur forms a colloidal solution which gradually coagulates.

$$H_2S_2O_3 = S + SO_2 + H_2O.$$

Its salts are also fairly easily decomposed by heat, leaving the corresponding sulphide and sulphate or the oxide and sulphide, free sulphur volatilizing at the same time. The thiosulphate ion is colourless.

Solubility. Of the thiosulphates which have been prepared most are soluble in water. Those of *silver*, *mercury*, and *lead* are insoluble and *barium thiosulphate* is only very slightly soluble in water.

Identification

With the dry salts.

1. Dilute hydrochloric acid decomposes thiosulphates, liberating *sulphur dioxide* (which can be driven off on warming) and depositing *sulphur*. Some of the sulphur remains in colloidal solution.

$$Na_2S_2O_3+2HCl = 2NaCl+H_2O+SO_2+S.$$

As with sulphites, concentrated sulphuric acid would liberate sulphur dioxide readily, but the reaction is not a specific test for thiosulphates.

With solutions.

2. (*a*) A neutral thiosulphate solution gives with barium nitrate solution a white precipitate of barium thiosulphate, soluble in dilute nitric acid with formation of sulphur by the usual decomposition. In order to make the original precipitate form, the solution should be agitated and left for a few minutes for the characteristic slow precipitation to finish.

(*b*) Calcium thiosulphate is relatively soluble and hence no precipitate is obtained with calcium nitrate solution.

3. Silver nitrate solution precipitates from a neutral thiosulphate solution white silver thiosulphate which is soluble in excess of the thiosulphate, and therefore excess silver nitrate must be added to ensure precipitation. The chief characteristic of the precipitate is its instability, which is shown by its rapid change of colour through yellow and brown to black. The final precipitate consists of black silver sulphide, and is insoluble in cold dilute nitric acid.

The solubility of the original precipitate in excess sodium thiosulphate solution is a property shared with other insoluble silver salts and accounts for the use of sodium thiosulphate in 'fixing' (i.e. dissolving out unaffected silver salts from) photographic negatives and prints.

Decomposition: $Ag_2S_2O_3+H_2O = Ag_2S+H_2SO_4$.

Complex formation:

$$Ag_2S_2O_3+Na_2S_2O_3 = 2Na[Ag(S_2O_3)].$$

Sulphates

Sulphuric acid H_2SO_4 is a colourless oily liquid of density 1·84 which is miscible with water with evolution of considerable heat. In mixing the two, the acid should always be poured into the water. (Pouring water on to the heavier acid results in the sudden generation of steam and acid spray which may cause damage.) Being dibasic, the acid forms normal and acid salts, e.g. Na_2SO_4 and $NaHSO_4$, and a great many double sulphates such as ferrous ammonium sulphate $FeSO_4.(NH_4)_2SO_4.6H_2O$ and the alums, e.g. potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$, are known. These salts are sometimes formulated as if they contained complex anions built up round a metallic atom, e.g. $K[Al(SO_4)_2]12H_2O$. Although such ions are formed by some metals, in most cases there is no evidence for their existence in solution, as the commoner double sulphates almost always give the reactions of the sulphate ion and of the simple metallic cations from which they are made up. The alum molecules are crystalline rather than chemical complexes.

The alkali sulphates and those of the alkaline earths are stable to heat. Most of the other sulphates decompose fairly readily on strong heating, giving off sulphur trioxide vapour and its dissociation products, sulphur dioxide and oxygen. The metallic oxide remains, unless decomposable by heat, e.g. $2CuSO_4 = 2CuO+2SO_2+O_2$. The sulphate ion SO_4'' and acid sulphate ion HSO_4' are colourless.

SOLUBILITY. Most of the sulphates are soluble, but those of *barium*, *strontium*, *lead*, and the *mercurous* ion are insoluble, while calcium sulphate is sparingly soluble in water. Some basic sulphates are insoluble also. The majority of the sulphates are hydrated.

Identification

With the dry salts.

1. Neither dilute hydrochloric acid nor concentrated sulphuric acid show any reaction with solid sulphates. Dehydration of coloured hydrates by concentrated sulphuric acid may cause colour changes but this is not necessarily confined to sulphates.

2. If the salt is mixed with powdered charcoal and heated strongly away from air (in the bottom of a hard-glass test-tube) the sulphate is reduced to the corresponding *sulphide* and shows the appropriate reactions (see p. 42).

With solutions.

3. (*a*) A solution of barium nitrate added to a neutral sulphate solution gives a fine, heavy, white precipitate of barium sulphate. This is insoluble in dilute or concentrated nitric acid.

(*b*) Calcium nitrate will only precipitate calcium sulphate from concentrated solutions of a sulphate. The precipitate is much less soluble in aqueous alcohol than in water, and alcohol may therefore be added to cause precipitation if necessary.

4. A neutral solution of a sulphate gives no precipitate with silver nitrate unless the sulphate is in high concentration, when a characteristic colourless crystalline precipitate of silver sulphate is formed.

Persulphates

Persulphuric acid $H_2S_2O_8$ is known in solution only; its salts are prepared from the potassium or ammonium salts either of which can be made by electrolysis of concentrated solutions of the corresponding sulphates. The ion S_2O_8'' is colourless.

SOLUBILITY. The persulphates which are known are soluble in water and decompose on warming with liberation of oxygen and free sulphuric acid. The oxygen contains ozone and by warming a solution of potassium persulphate with dilute nitric acid a vigorous evolution of richly ozonized oxygen is obtained.

Identification

With the dry salts.

1. Dilute hydrochloric acid liberates oxygen and ozone. The latter, which is a colourless gas, may be recognized by its peculiar smell and its power of liberating iodine from potassium iodide (turning starch iodide paper blue).

$$O_3+2KI+H_2O = O_2+2KOH+I_2.$$

2. Concentrated sulphuric acid forms permonosulphuric acid (Caro's acid) H_2SO_5, but shows no visible reaction.

With solutions.

3. Barium nitrate solution gives no immediate precipitate with a solution of a persulphate but a precipitate of barium sulphate forms as the persulphate decomposes.

4. (*a*) When silver nitrate solution is added to a solution of a persulphate, black silver peroxide is precipitated. With ammonium persulphate some nitrogen may be evolved.

$$2AgNO_3+K_2S_2O_8+2H_2O = 2KNO_3+2H_2SO_4+Ag_2O_2.$$

(*b*) Nickel ions cause no precipitate with persulphate ions.

Acids of Nitrogen, Phosphorus, Arsenic, and Antimony

The normal hydrides of these elements (ammonia NH_3, phosphine PH_3, arsine AsH_3, stibine SbH_3) are basic rather than acidic, and do not give rise to true salts by the replacement of hydrogen. The nitrides, phosphides, arsenides, and antimonides are usually decomposed by water to give the corresponding hydride. (The marked decrease in acid character from HCl to H_2S and thence to H_3P should be noted.)

In the formation of oxyacids nitrogen shows little similarity to the other members of the group (cf. fluorine in the halogen group), while arsenic and antimony, although giving fewer acids than phosphorus, show at any rate a formal resemblance to this element.

The Nitrogen Acids

The important oxyacids of nitrogen are NITROUS ACID HNO_2 and NITRIC ACID HNO_3.

An unimportant and unstable hyponitrous acid $H_2N_2O_2$ is known, and the explosive hydrazoic acid HN_3, whose salts, the azides, are also liable to detonate, must be regarded as a nitrogen acid.

Nitrites

Free nitrous acid is extremely unstable and decomposes rapidly on formation at ordinary temperatures into water, nitric oxide NO, and nitrogen peroxide NO_2, through the intermediate stage of nitrogen trioxide N_2O_3.

$$2HNO_2 = H_2O+N_2O_3 = H_2O+NO+NO_2.$$

All nitrites except those of the alkali metals are decomposed on heating, the oxide of the metal eventually remaining (unless also decomposed by heat), but the decomposition is not always a simple one, nitrates and basic nitrites being formed at first. Ammonium nitrite gives nitrogen and water on heating. The nitrite ion is colourless.

SOLUBILITY. The nitrites are all soluble in water. The silver salt is only sparingly soluble in water while the barium salt is extremely soluble.

Identification

With the dry salts.

1. Dilute hydrochloric acid decomposes all nitrites, forming nitrous anhydride N_2O_3 which gives a blue colour to the solution (more noticeable if the solution is kept ice-cold) and liberating the decomposition products of this compound, *nitric oxide* NO and *nitrogen peroxide* NO_2 (see above). The nitric oxide unites with the oxygen in the air to form more nitrogen peroxide, which can be recognized by its brown colour, solubility in water, and acid character.

The reaction with sulphuric acid is similar but very violent and unnecessary as a test for nitrites.

With solutions.

2. Barium nitrate is itself much less soluble than the nitrite and therefore no precipitate is formed when a neutral nitrite is treated with this reagent. Calcium nitrite is also soluble.

3. A *concentrated* neutral solution of a nitrite will give a crystalline precipitate of silver nitrite when treated with silver nitrate solution. The precipitate is readily decomposed by dilute nitric acid with evolution of nitric oxide and nitrogen peroxide.

4. If ferrous sulphate solution be added to a solution of a nitrite and the mixture acidified with dilute acetic acid, the nitric oxide liberated will give its characteristic brown coloration with the ferrous sulphate.

$$2CH_3COOH + 2NaNO_2 = 2NaOOC{\cdot}CH_3 + H_2O + NO + NO_2$$

$$NO + FeSO_4 = [Fe(NO)]SO_4.$$

This is similar to the brown ring test for nitrates (see **Nitrates 4**), but the brown colour is developed as soon as the nitrite solution becomes faintly acid, whereas concentrated sulphuric acid is needed for the nitrate test. As bench solutions of ferrous sulphate are usually made up in dilute sulphuric acid, acetic acid is often unnecessary.

5. A solution containing a nitrite will decolorize acidified potassium permanganate solution. The nitrite is oxidized to the corresponding nitrate.

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 = 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

6. If a small quantity of a nitrite solution be added to potassium iodide solution, and acidified with dilute acetic acid, iodine is set free. In this case the nitrous acid liberated is reduced to nitric oxide.

$$2HNO_2 + 2KI + 2CH_3COOH = 2CH_3COOK + 2H_2O + I_2 + 2NO.$$

7. Free nitrous acid can be destroyed by boiling its solution with urea. Nitrogen and carbon dioxide are evolved.

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2.$$

Nitrates

Nitric acid HNO_3 is a colourless liquid, which is often discoloured by the products of its decomposition or reduction. The acid and solutions of the acid in water are powerful oxidizing agents, but this is largely a property of the acid molecule rather than of the nitrate ion which is comparatively stable. The oxide which corresponds to nitric acid is the unstable solid nitrogen pentoxide N_2O_5.

All nitrates are decomposed on heating, the mode of decomposition depending upon the metallic radical present. Most of them give off oxygen and nitrogen peroxide NO_2 and leave the oxide of the metal (or the metal itself if the oxide is decomposed by heat): e.g.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$
$$Hg(NO_3)_2 = Hg + 2NO_2 + O_2.$$

The nitrates of the alkali metals melt on heating and eventually give off oxygen, leaving the corresponding nitrite:

$$2KNO_3 = 2KNO_2 + O_2.$$

Ammonium nitrate decomposes into nitrous oxide and steam:

$$NH_4NO_3 = N_2O + 2H_2O.$$

The nitrate ion is colourless.

SOLUBILITY. All normal nitrates are soluble in water, but bismuth and mercury form insoluble basic salts.

Identification

With the dry salts.

1. Dilute hydrochloric acid has no obvious effect upon a nitrate.

2. Concentrated sulphuric acid has no obvious effect upon a nitrate in the cold, but liberates nitric acid which can be distilled with partial decomposition at a moderately high temperature. The acid can be recognized by the brown fumes of nitrogen peroxide which accompany it.

$$H_2SO_4+KNO_3 = KHSO_4+HNO_3$$
$$4HNO_3 = 2H_2O+4NO_2+O_2.$$

This reaction should be compared carefully with that given by bromides (**Halides 2**).

With solutions.

3. As all inorganic nitrates are soluble, nitrate ions show no characteristic precipitation reactions with cations.

4. If *freshly made* ferrous sulphate solution be added to a solution of a nitrate in a test-tube, and concentrated sulphuric acid poured cautiously down the side of the tube so that it forms a layer at the bottom of the tube, a brown ring is formed at the junction of the two layers. (Alternatively, the acid may be mixed with the nitrate solution and the ferrous sulphate added carefully to form a layer on the top of the mixture.)

The formation of the brown ring is due to the following reactions: (i) the liberation of nitric acid from the nitrate by the action of the sulphuric acid; (ii) the reduction of the *nitric acid* by the ferrous ion to form nitric oxide (note that ferrous sulphate does not reduce the nitrate ion)

$$6H^{\cdot}+2HNO_3+6Fe^{\cdot\cdot} = 6Fe^{\cdot\cdot\cdot}+4H_2O+2NO;$$

(iii) the union of the nitric oxide and ferrous sulphate to form the brown compound $[Fe(NO)]SO_4$.
Contrast these reactions with the behaviour of nitrites (**Nitrites 4**).

5. Nitrates are reduced in alkaline solution by aluminium, zinc or, better, Devarda's alloy, with formation of ammonia gas which is expelled on warming the alkaline solution.

$$NaNO_3+4Zn+7NaOH = 4Na_2ZnO_2+2H_2O+NH_3.$$

The Phosphorus Acids

Like its neighbours in the Periodic Table phosphorus forms numerous acids, those derived from the pentoxide P_2O_5 being most important. These are:

ORTHOPHOSPHORIC ACID $H_3PO_4 = [P_2O_5+3H_2O]$.
PYROPHOSPHORIC ACID $H_4P_2O_7 = [P_2O_5+2H_2O]$.
METAPHOSPHORIC ACID $HPO_3 = [P_2O_5+H_2O]$.

Metaphosphoric acid corresponds formally to nitric acid HNO_3, but its properties are very different from those of nitric acid. The acid corresponding to the trioxide, PHOSPHOROUS ACID H_3PO_3, is not at all similar to nitrous acid for it is actually a dibasic acid $H_2(HPO_3)$ with a strong reducing action, and both the acid and its salts decompose on heating in a comparatively complex manner. Of the other acids of phosphorus, the monobasic HYPOPHOSPHOROUS ACID $H(H_2PO_2)$ and its salts are of some interest. The analytically important characteristics of phosphites and hypophosphites are summarized below.

Phosphites and hypophosphites

1. *Ignition.* The ultimate decomposition products in both cases are the corresponding phosphate and the gas *phosphine* PH_3 which can be recognized by its smell and action on silver nitrate (p. 29).

2. *Action of acids on the dry salts.* Dilute hydrochloric acid shows no reaction but concentrated sulphuric acid is reduced on warming with either type of salt to sulphur dioxide.

3. Barium hypophosphite is soluble; barium phosphite is insoluble in water but readily soluble in dilute nitric acid. Calcium phosphite is soluble in acetic acid.

4. Silver nitrate solution is reduced to metallic silver by a solution of a hypophosphite, especially on warming, yellow silver phosphate being formed simultaneously. A solution of a phosphite gives first a white precipitate of silver phosphite which then changes to metallic silver and silver phosphate.

5. By the action of zinc in sulphuric acid solution both phosphites and hypophosphites are reduced to phosphine.

Phosphates

When phosphorus pentoxide dissolves in water the first product is a solution of metaphosphoric acid. If this solution is boiled orthophosphoric acid is formed. If anhydrous orthophosphoric acid or its concentrated solution is heated to about 250° C., then pyrophosphoric acid is formed. On further heating this loses more water and returns to metaphosphoric acid.

As a rule, when oxyacids of an element differ only in the amount of water they contain, a solution of any one of the acids will contain appreciable quantities of the ions of the other acids in equilibrium. For instance, there is no difference between a solution of sulphuric acid $H_2SO_4[= 2H^{\cdot}+SO_4'']$ and a solution of pyrosulphuric acid $H_2S_2O_7$ (obtained by distilling hydrated ferrous sulphate)

$$H_2O+H_2S_2O_7 = H_2O+2H^{\cdot}+S_2O_7'' = 4H^{\cdot}+2SO_4''.$$

In the case of the phosphoric acids the change is so slow that independent reactions are observable for the three anions PO_4''', PO_3', and P_2O_7''''.

It should be noticed that orthophosphoric and pyrophosphoric acids can give rise to acid salts, e.g. Na_2HPO_4. The acid orthophosphates are converted to pyrophosphates or metaphosphates on ignition.

$$2Na_2HPO_4 = Na_4P_2O_7+H_2O$$

$$NaH_2PO_4 = NaPO_3+H_2O.$$

Otherwise the simple phosphates are stable to heat. Phosphates containing the ammonium radical are, however, decomposed, leaving metaphosphoric acid in the case of normal ammonium phosphate or the pyrophosphate of any other metallic radical present. The ions of all the phosphoric acids are colourless.

Solubility. All normal phosphates, except those of the alkali metals and ammonium, are insoluble in water; the primary acid phosphates are soluble, however, and they are formed when a normal phosphate dissolves in a strong acid (see p. 10). (Cf. solubility of bicarbonates, bisulphites,

&c.) The soluble normal phosphates are hydrolysed and show an alkaline reaction owing to the weak acid character or small dissociation of phosphoric acid. In the case of the alkali phosphates only salts of the sodium dihydrogen phosphate type, NaH_2PO_4, show any approach to acidity.

Identification

With the dry salts.

1. Neither dilute hydrochloric acid nor concentrated sulphuric acid give any visible reaction with a phosphate.

With solutions.

2. (*a*) A solution of barium nitrate added to a neutral solution of any phosphate gives a white precipitate of the appropriate barium salt, soluble in dilute nitric acid.

(*b*) Calcium nitrate precipitates white calcium phosphate, soluble in acetic acid.

3. A solution of silver nitrate added to a neutral solution of:

(*a*) an orthophosphate, gives a *yellow* precipitate of *normal* silver orthophosphate Ag_3PO_4;

(*b*) a metaphosphate or pyrophosphate, gives a *white* precipitate of the corresponding silver salt.

These precipitates are all soluble in dilute nitric acid.

When neutral disodium hydrogen phosphate reacts with precipitating agents such as silver nitrate, some phosphate must be left in solution.

$$2Na_2HPO_4+3AgNO_3 = Ag_3PO_4+3NaNO_3+NaH_2PO_4$$

or, ionically, $2HPO_4''+3Ag^{\cdot} = Ag_3PO_4+H_2PO_4'$.

It is obviously wrong to write the equation:

$$Na_2HPO_4+3AgNO_3 = Ag_3PO_4+2NaNO_3+HNO_3$$

as the nitric acid would immediately dissolve some of the silver phosphate.

4. A solution of ammonium molybdate in nitric acid added to a *relatively small quantity* of any phosphate (preferably dissolved in nitric acid also) gives with *gentle* *warming*, if necessary, a crystalline yellow precipitate of ammonium phosphomolybdate. Excess of the molybdate is required as the precipitate consists of a compound of *twelve* molecules of molybdic anhydride MoO_3 with one molecule of ammonium phosphate $(NH_4)_3PO_4$ and probably two molecules of water, $(NH_4)_3H_4[P(Mo_2O_7)_6]$.

5. Ferric chloride solution precipitates from solutions which contain phosphates pale yellow ferric phosphate, insoluble in acetic acid.

This reaction is made use of in the removal of phosphoric acid when it interferes with the normal course of cation analysis. As ferric phosphate is appreciably soluble in ferric acetate solution it is important not to have too great an excess of ferric ion present when phosphate has to be removed.

Distinction between ortho-, meta-, and pyrophosphates

(*a*) The orthophosphates are recognized by the yellow colour of the silver orthophosphate precipitate.

(*b*) A solution of a metaphosphate acidified with acetic acid (i.e. free metaphosphoric acid) coagulates a solution of albumen in the cold.

(*c*) A solution of a pyrophosphate similarly acidified will not coagulate albumen in the cold.

The Arsenic Acids

The principal acids formed by arsenic are similarly constituted to the corresponding phosphorus acids, but they are weaker acids and their reactions in solution show fewer variations.

ARSENIOUS ACID H_3AsO_3 is derived from the trioxide As_4O_6 and is tribasic (contrast $H_2(HPO_3)$ dibasic, and HNO_3 monobasic).

ARSENIC ACID H_3AsO_4 is derived from the pentoxide As_4O_{10} and is also tribasic. Salts of the meta- and pyro-forms of both acids are known, but in solution they all give identical reactions (contrast the phosphates). The ions of both acids are colourless.

Arsenites

Arsenious acid H_3AsO_3 has been prepared only in aqueous solution. The anhydride is very sparingly soluble in water but quite soluble in the hydroxides of the alkali metals forming arsenites. ($As_4O_6 + 12KOH = 6H_2O + 4K_3AsO_3$.) The arsenites of the heavy metals are decomposed by heat, arsenic trioxide volatilizing away.

SOLUBILITY. Arsenites other than those of the alkali metals are insoluble in water, but are readily soluble in acids (cf. phosphates).

Identification

With the dry salts.

1. There is no visible reaction between dilute hydrochloric, acid, or concentrated sulphuric acid and an arsenite.

With solutions.

2. (*a*) When added to a neutral solution of an arsenite, barium nitrate solution precipitates colourless barium arsenite, which is readily dissolved by nitric acid.

(*b*) Calcium nitrate solution gives a similar precipitate soluble in acetic acid.

3. Neutral solutions of arsenites give with silver nitrate solution a bright yellow precipitate of silver arsenite Ag_3AsO_3, soluble with ease in dilute nitric acid.

4. If a few drops of copper sulphate solution be added to an arsenite solution acidified with hydrochloric acid, and potassium hydroxide added cautiously, a green precipitate is formed. This is copper pyroarsenite or Scheele's green and may be formulated as $CuHAsO_3$ or $Cu_2As_2O_5$. It is soluble in excess alkali hydroxide and the initial acid is required to prevent the solution from becoming alkaline. The precipitate appears when enough potassium hydroxide has been added to make the solution exactly neutral. If excess alkali is added and the solution heated, a red precipitate of cuprous oxide is formed, the arsenite acting as a reducing agent.

$$K_3AsO_3 + CuSO_4 + H_2O = CuHAsO_3 + K_2SO_4 + KOH$$

$$2CuHAsO_3 + 2KOH = K_2[Cu_2(As_2O_6)] + 2H_2O$$

$$K_2[Cu_2(As_2O_6)] + 4KOH = K_3AsO_3 + K_3AsO_4 + Cu_2O + 2H_2O.$$

5. Owing to the amphoteric character of arsenious oxide, a solution of an arsenite acidified with hydrochloric acid shows the reactions of the *positive* arsenic ion, owing to the equilibrium:

$$AsO_3''' + 6H^\cdot = As^{\cdot\cdot\cdot} + 3H_2O.$$

Arsenates

The compound H_3AsO_4, orthoarsenic acid, is a colourless solid which decomposes on heating to give pyroarsenic acid $H_4As_2O_7$, metarsenic acid $HAsO_3$ and ultimately the anhydride As_2O_5. The acids are all soluble in water, but in solution show no distinction in their ionic reactions (contrast phosphates). The salts are less stable to heat than the phosphates, giving off oxygen and forming the corresponding arsenite in the case of the alkali metals, while the rest yield oxygen and arsenious oxide, leaving a metallic oxide residue.

SOLUBILITY. All normal arsenates except those of the alkali metals are insoluble in water. They dissolve in acids to form acid salts and undissociated arsenic acid (cf. phosphates). The soluble arsenates are hydrolysed and the normal salts have an alkaline reaction in aqueous solution. (The similarity of the phosphates to the arsenates led to the discovery of the *law of isomorphism.*)

Identification

With the dry salts.

1. Neither dilute hydrochloric acid nor concentrated sulphuric acid shows any reaction with arsenates.

With solutions.

2. (*a*) With a neutral solution of an arsenate, barium nitrate solution gives a white precipitate of barium arsenate, soluble in dilute nitric acid.

(*b*) Calcium nitrate solution gives a similar precipitate soluble in acetic acid.

3. Silver nitrate solution gives with an arsenate a 'terra-cotta' precipitate of silver arsenate soluble in dilute nitric acid. (In a neutral solution the acid-salt ions will be present and the equation will be similar to that given in **Phosphates 3.**)

4. A solution of an arsenate added to excess of ammonium molybdate solution in nitric acid gives *on boiling* a yellow precipitate of ammonium arsenomolybdate. (The corresponding phosphate precipitate (q.v.) forms at 60° C. or below.)

Acids of Antimony and Bismuth

ANTIMONY forms acids and salts similar to those of arsenic but they are not at all common. The most important reaction of these salts is given under Sodium (**Na 1**). BISMUTH forms no acids in its trivalent state, but unstable 'bismuthates' of the alkali metals are known.

The Acids of Carbon and Silicon

Carbides and silicides are not salts, but are related to the gases methane CH_4, acetylene C_2H_2, and silicon hydride which are non-acidic. The only acidic oxides of carbon and silicon are the normal oxides, carbon dioxide CO_2 and silica SiO_2, and these give rise to the acids CARBONIC ACID H_2CO_3 and SILICIC ACID H_2SiO_3 which are presumed to exist in solution (in the case of silicic acid in colloidal solution). Carbonates are all derived from the simple acid H_2CO_3. Silicates on the other hand are derived from very complex acids containing varying relative quantities of silica and water. These complex silicates constitute a large part of the earth's crust and are usually very insoluble even when they contain the alkali metals as cations. Carbon forms many other acids also, but these are quite distinct from carbonic acid and belong to the province of organic chemistry: a few are discussed below.

Carbonates and many silicates are readily broken up by acids as the free acid is in each case unstable. There is in solution the equilibrium

$$H_2CO_3 \rightleftharpoons H_2O+CO_2 \text{ or } H_2SiO_3 \rightleftharpoons H_2O+SiO_2.$$

With carbonic acid the anhydride escapes as a gas and displaces the equilibrium towards the right (cf. sulphites, nitrites). In the case of the silicates, silica separates (often very slowly if cold) as a very insoluble solid, and again displaces the equilibrium to the right. The identification of silicates is therefore usually an identification of the liberated silica (see p. 157). A few analytical reactions of silicates and a fuller study of carbonates is given below. For details of the analysis of refractory silicates a larger text-book must be consulted.

Ammonium silicate does not exist, but silicates of most of the metals are known. Those of the alkali metals are soluble, but are hydrolysed and therefore alkaline in solution.

Aluminium, tin, arsenic, and antimony do not form carbonates; bismuth and mercury form only basic carbonates.

As carbonic acid is dibasic, bicarbonates can be formed; those of the alkali metals can be isolated, those of the alkaline earths exist in solution (i.e. the insoluble carbonates of the alkaline earths dissolve in water containing carbon dioxide). Bicarbonates of the heavy metals probably do not exist to any appreciable extent.

Heat has no effect as a rule on silicates. Bicarbonates are all decomposed to give the corresponding carbonate (which may decompose further as described below), carbon dioxide, and water:

$$2KHCO_3 = K_2CO_3+H_2O+CO_2.$$

Carbonates of the alkali metals *do not decompose on heating*. Ammonium carbonate breaks up at a very low temperature into ammonia, water, and carbon dioxide:

$$(NH_4)_2CO_3 = 2NH_3+H_2O+CO_2.$$

All other carbonates decompose to give the oxide of the metal and carbon dioxide. The weaker the base the more readily is the carbonate split up. The oxides of 'noble' metals may be further decomposed.

Solubility. The carbonates and silicates of the alkali metals are soluble. Ammonium carbonate is also soluble in water. All the other normal salts of these acids are insoluble. Bicarbonates of calcium, strontium, barium, magnesium, and possibly iron exist in solution. The bicarbonates of the alkali metals are soluble, but less soluble than the normal carbonates.

Identification

(*a*) Carbonates

With the dry salts.

1. Dilute hydrochloric acid decomposes all carbonates with evolution of *carbon dioxide.* The gas is recognized by its power of precipitating calcium carbonate from lime water (calcium hydroxide solution):

$$CO_2+Ca(OH)_2=CaCO_3+H_2O.$$

Fill a clean test-tube nearly full with *clear* lime water, and allow the evolved gas to pour on to the surface of the liquid. Then give the lime water a very slight shake and rings of the white precipitate will be seen below the meniscus.

With solutions.

Of those which we are considering here only the alkaline carbonates are soluble. If a 'neutral solution' of an insoluble substance be made by double decomposition with sodium carbonate and subsequent treatment with acid (see p. 13), there is clearly no point in testing for an original carbonate in that solution, although it is important to know what the effect of the presence of undecomposed carbonate will be.

2. (*a*) Barium nitrate solution precipitates from a solution of a carbonate white barium carbonate which is decomposed by dilute nitric acid.

(*b*) Calcium nitrate solution gives a similar precipitate soluble in acetic acid.

3. Silver nitrate solution precipitates from a neutral solution of a carbonate white silver carbonate (which may become yellow). It is decomposed by dilute nitric acid with evolution of carbon dioxide, and is partly decomposed on heating with water.

4. Distinction is made between alkali carbonates and bicarbonates by the effect of heat on the dry salts or their solutions.

(*b*) **Silicates**

With the dry salts.

1. Neither dilute hydrochloric acid nor concentrated sulphuric acid shows any visible reaction with silicates.

2. When a silicate is mixed with sodium fluoride and treated in a lead or iron crucible (*not glass*) with concentrated sulphuric acid silicon tetrafluoride SiF_4 is formed. If a moist watch glass with a drop of water hanging from the convex surface be placed over the crucible for a few seconds the silicon tetrafluoride will be hydrolysed to silicon dioxide which will form a skin on the drop. The watch glass should not be left long enough for the hydrogen fluoride formed to attack the glass (cf. **Halides 5**).

With solutions.

3. (*a*) Barium nitrate solution precipitates from solutions of silicates white barium silicate which is soluble in dilute nitric acid.

(*b*) Calcium nitrate solution gives a similar precipitate soluble in acetic acid.

(*c*) **Fluosilicates**

These are characterized by the following reactions:

1. They give silicon tetrafluoride on treatment with concentrated sulphuric acid without previous admixture of either silica or sodium fluoride:

$$Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + 2HF + SiF_4.$$

2. Barium nitrate solution gives a white gelatinous precipitate insoluble in dilute nitric acid. The precipitate is quite unlike barium sulphate in appearance. Calcium nitrate solution gives a similar precipitate, insoluble in dilute acetic acid.

3. Silver nitrate solution gives no precipitate.

The Cyanogen Acids

These include HYDROCYANIC ACID (prussic acid) HCN, CYANIC ACID HCNO, THIOCYANIC ACID HCNS, and the acids whose anions consist of cyanide radicals attached to a metallic atom, the most important of which are FERROCYANIC ACID $H_4[Fe(CN)_6]$ and FERRICYANIC ACID $H_3[Fe(CN)_6]$. The chemistry of these acids is connected with that of the gas cyanogen $(CN)_2$ which behaves in some respects rather like a halogen. The gas and most of its derivatives are **very poisonous** and great care should be taken in handling them.

The free acids mentioned above are comparatively unimportant, but some of their salts are extremely useful substances. *Hydrocyanic acid* is a colourless liquid (b. pt. 26·5°) with a smell like that of bitter almonds. *Cyanic acid* is a very volatile liquid which polymerizes rapidly to cyamelide $(HCNO)_n$ or to cyanuric acid $(HCNO)_3$. It is hydrolysed in solution to ammonium bicarbonate: $2H_2O+HCNO = NH_4HCO_3$. *Thiocyanic acid* is an unstable liquid, while the acids of the complex metal cyanides are solids which decompose readily.

Simple *cyanides* of monovalent and divalent cations only are known. Those of trivalent radicals are immediately converted into complex cyanides on formation. Most insoluble cyanides are soluble in excess of potassium cyanide solution and form complexes of a wide range of stability. In some the complex is dissociated in water and gives, therefore, the reactions of its constituent ions; e.g. the equilibrium

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^{\cdot}+[Cd(CN)_4]'' \rightleftharpoons 2K^{\cdot}+Cd^{\cdot\cdot}+4CN'$$

is largely over towards the right-hand side and the complex is readily decomposed by acids in consequence. In others, such as the ferrocyanides (e.g. $K_4[Fe(CN)_6]$), the complex ion is practically unaffected by water or acids.

Comparatively few *cyanates* are known.

STABILITY. The alkali *cyanides* are stable to heat if kept dry and free from oxygen (otherwise they are hydrolysed or are partially oxidized to cyanate). Those of the 'noble' metals (Ag, Hg) give off cyanogen and leave the metal; the remainder give off nitrogen and leave a metallic carbide or a mixture of metal and carbon.

The alkali *cyanates* are stable if dry, otherwise they are hydrolysed to the corresponding carbonates. Ammonium cyanate changes to urea on heating: $NH_4CNO = CO(NH_2)_2$.

The alkali *thiocyanates* are also stable and show remarkable colour changes on fusion, turning yellow, brown, green, blue, and white again on cooling. The decomposition of other cyanates, thiocyanates, and complex cyanides is too complex to be discussed here.

SOLUBILITY. The alkali metals and alkaline earth metals form soluble salts with all five acids. Except for the thiocyanates, *mercuric cyanide*, and possibly *ferric ferricyanide*, the salts of other cations with these acids are insoluble. The *thiocyanates* somewhat resemble the chlorides in solubility, the *silver*, *mercury*, and *cuprous* salts being insoluble and the lead salt soluble with difficulty. (Note, however, that the *mercuric* salt, as well as the *mercurous* salt, is practically insoluble.)

Identification

Note. *Mercuric cyanide* $Hg(CN)_2$ though soluble in water is a non-electrolyte and does not give the ionic reactions of cyanides.

With the dry salts.

1. Of the salts of these five acids, only the *cyanates* give a visible reaction with dilute hydrochloric acid as the cyanic acid liberated is hydrolysed to ammonium bicarbonate and decomposed.

$$KCNO + 2HCl + H_2O = NH_4Cl + KCl + CO_2.$$

An acidified solution of a *cyanide* (except mercuric cyanide) smells of hydrocyanic acid. Thiocyanates, ferrocyanides, and ferricyanides show no reaction.

2. Hot concentrated sulphuric acid liberates *carbon monoxide* (see p. 29) from *cyanides*, *ferrocyanides*, and *ferricyanides*. The reaction may be regarded as (*a*) the liberation of hydrocyanic acid HCN:

$$H_2SO_4 + 2KCN = K_2SO_4 + 2HCN;$$

(*b*) the hydrolysis of this acid to ammonium formate (a common type of reaction in organic chemistry); and (*c*) the dehydration of the formic acid liberated from this product.

$$HCN + 2H_2O = H{\cdot}COONH_4$$

$$2H{\cdot}COONH_4 + H_2SO_4 = (NH_4)_2SO_4 + 2CO + 2H_2O.$$

From *cyanates* (which contain one more oxygen atom than cyanides) carbon dioxide is liberated by a similar process (hydrolysis to carbonate followed by decomposition). From *thiocyanates* (which contain an atom of sulphur more than the cyanides) the evil-smelling *carbon oxysulphide* COS is liberated along with carbon dioxide and sulphur dioxide; sulphur is deposited.

With solutions.

3. Neither barium nor calcium ions give any precipitate with these anions as the alkaline earth salts are all soluble.

4. Nickel nitrate solution gives precipitates of the corresponding nickel salts with the following neutral solutions:

(*a*) *cyanide*: a pale green precipitate soluble in excess of potassium cyanide.

(*b*) *ferrocyanide*: a very pale bluish green precipitate.

(*c*) *ferricyanide*: a brown precipitate.

It gives no precipitate with cyanates or thiocyanates.

5. Silver nitrate solution added to a neutral solution of a *cyanide*, *ferrocyanide*, or *thiocyanate* gives a *white* precipitate, and added to a neutral solution of a *ferricyanide* gives an *orange* precipitate of the corresponding silver salt, all of which are insoluble in dilute nitric acid. Cold concentrated nitric acid oxidizes silver ferrocyanide to silver ferricyanide. *Cyanates* give with silver nitrate solution a *white* precipitate which like all cyanates is decomposed by dilute nitric acid. The precipitate of silver cyanide is readily soluble in excess potassium cyanide solution:

$$AgCN + KCN = K[Ag(CN)_2].$$

6. The addition of ferric chloride solution enables a distinction to be made between the following:

(*a*) a *ferrocyanide* gives a Prussian blue precipitate of ferric ferrocyanide.

(*b*) a *ferricyanide* gives no precipitate but a brown solution, assumed to contain ferric ferricyanide.

(*c*) a *thiocyanate* gives a blood-red coloration due to ferric thiocyanate which can be extracted with ether.

Note that ferrous compounds give an intense blue precipitate with a ferricyanide solution.

7. A very sensitive test for *ferrocyanides* is the chocolate-brown precipitate of copper ferrocyanide formed by the addition of copper sulphate solution.

8. In the absence of ferrocyanides or thiocyanates the presence of *cyanide* ion may be confirmed by conversion to either of these, and the more sensitive tests for these ions applied. Addition of ferrous sulphate to an alkaline solution of the cyanide produces a ferrocyanide; evaporating to dryness *in a fume cupboard* with yellow ammonium sulphide produces a thiocyanate.

The Common Organic Acids

These acids are all characterized by the grouping of atoms $-\mathrm{C}\begin{array}{l}/\!\!/\mathrm{O}\\ \diagdown\mathrm{OH}\end{array}$. The following salts are described here:

FORMATES, ACETATES, OXALATES, TARTRATES. *Formic acid* H·COOH is a colourless, poisonous liquid (m.pt. 8°, b.pt. 100°) with a rather unpleasant penetrating smell. *Acetic acid* CH_3·COOH is solid below 16° and boils at 118°. It is colourless and has the smell of vinegar, which contains it. *Oxalic acid* $\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$ and *tartaric acid* $\begin{array}{l}\mathrm{CH(OH)COOH}\\ |\\ \mathrm{CH(OH)COOH}\end{array}$ are colourless crystalline solids. All four acids are soluble in water. For further details of their preparation and properties organic text-books must be consulted.

The residue after heating the salts of any of these acids is the carbonate or oxide of the metal concerned or the metal itself, according to their relative stability; e.g. carbonates are left by the alkali metal and alkaline earth salts, oxides by the heavy metals, and metals themselves only when their oxides are readily decomposed by heat. Formates and acetates give off organic vapours (mainly aldehydes and ketones) on heating; e.g.

$$Ca(OOC{\cdot}CH_3)_2 = CaCO_3 + CH_3{\cdot}CO{\cdot}CH_3 \text{ (acetone)}.$$

Oxalates give off carbon monoxide, a neutral gas burning with a blue flame to give carbon dioxide:

$$(NaOOC)_2 = Na_2CO_3 + CO.$$

Tartrates char on heating and smell like burnt sugar. Ammonium formate and acetate volatilize; ammonium oxalate gives off cyanogen and steam:

$$(NH_4OOC)_2 = 4H_2O + (CN)_2;$$

ammonium tartrate leaves a residue of carbon only.

Solubility. The formates and acetates are soluble as a rule. Silver acetate is only sparingly soluble, while the silver and lead salts are amongst the least soluble formates. The oxalates and tartrates of the alkali metals are soluble, otherwise these two anions form insoluble or very sparingly soluble salts. The acid tartrates of potassium and ammonium have remarkably low solubilities also.

Identification

With the dry salts.

1. In no case is there any visible reaction with dilute hydrochloric acid, but with formates and acetates the smell of the free acid is sometimes perceptible on warming.

2. With hot concentrated sulphuric acid and

(*a*) *acetates*: the free acid is liberated. The addition of ethyl alcohol to the substance before treatment with the acid causes the liberation of *ethyl acetate* which has a pleasant fruity smell much more distinctive than that of acetic acid;

(*b*) *formates*: *carbon monoxide* only is liberated which burns with a blue flame to form carbon dioxide (see p. 29):

$$2NaOOCH+H_2SO_4 = Na_2SO_4+2H_2O+2CO;$$

(*c*) *oxalates*: *carbon monoxide* and *carbon dioxide* are liberated:

$$(NaOOC)_2+H_2SO_4 = Na_2SO_4+H_2O+CO+CO_2.$$

In (*b*) and (*c*) the sulphuric acid acts as a dehydrating agent to the liberated acids.

(*d*) *tartrates*: *charring* occurs and gases containing *carbon monoxide*, *carbon dioxide*, and *sulphur dioxide* are given off. Sulphuric acid is reduced by tartrates.

With solutions.

3. Barium nitrate solution gives with neutral solutions of

(*a*) *formates* and *acetates*: no precipitate;

(*b*) *oxalates* and *tartrates*: a white precipitate soluble in dilute nitric acid.

4. Calcium nitrate solution gives white precipitates of the calcium salts with neutral solutions of oxalates and tartrates; of these calcium tartrate is soluble in acetic acid, while calcium oxalate is insoluble in acetic acid but is soluble in dilute hydrochloric acid.

5. (*a*) Nickel nitrate solution produces no precipitate with neutral solutions of formates or acetates.

(*b*) Ferric chloride solution gives a red coloration with neutral solutions of acetates and formates. On warming the solutions the corresponding basic salts are precipitated: e.g. basic ferric acetate.

6. Silver nitrate solution produces in all cases by double decomposition a white precipitate soluble in dilute nitric acid. The precipitate in the case of *acetates* is formed only in concentrated solution. That given by *formates* rapidly turns black owing to the reducing action of the formate ion and the formation of metallic silver.

7. A solution of an *oxalate* acidified with dilute sulphuric acid reduces a solution of potassium permanganate, decolorizing it:

$$5(COOH)_2+2KMnO_4+3H_2SO_4$$
$$= K_2SO_4+2MnSO_4+8H_2O+5CO_2.$$

8. If silver nitrate solution be added to a neutral solution of a *tartrate* in a test-tube and ammonium hydroxide added so that the precipitate almost entirely redissolves, a mirror of metallic silver is deposited on the walls of the test-tube on warming. (An oxalate will not reduce ammoniacal silver nitrate.)

Acids of Boron

Boron trioxide B_2O_3 gives rise to three acids, ORTHOBORIC ACID H_3BO_3, METABORIC ACID HBO_2, and PYROBORIC ACID $H_2B_4O_7$. No salts of orthoboric acid are known; most of the commoner borates are metaborates, but 'borax' is the decahydrated pyroborate of sodium, $Na_2B_4O_7\ 10H_2O$. Perborates, which may be regarded as the derivatives of PERBORIC ACID HBO_3, are also known, and 'perborax' is used extensively as an oxidizing agent in cleansers. The borate ion is colourless but the borates of coloured cations are used to identify those cations in the borax bead tests (see p. 136). The borates are stable to heat in the absence of water.

SOLUBILITY. The alkali metal borates are soluble in water and are hydrolysed to give an alkaline solution; the remainder are practically insoluble.

Identification

With the dry salts.

1. Neither dilute hydrochloric acid nor concentrated sulphuric acid shows any visible reaction with a borate, as boric acid is stable and non-volatile (cf. phosphates).

2. If the solid borate be mixed with a little concentrated sulphuric acid, and alcohol (preferably methyl alcohol) added, on setting light to the alcohol a green-edged flame is obtained. The colour is characteristic of boric acid and is due to the presence of volatile methyl borate $B(OCH_3)_3$ in the flame.

With solutions.

3. (*a*) When added to a neutral solution of a borate, barium nitrate solution gives a white precipitate of barium metaborate, soluble in dilute nitric acid with ease.

$$Ba(NO_3)_2+Na_2B_4O_7+3H_2O = Ba(BO_2)_2+2H_3BO_3+2NaNO_3.$$

If barium chloride solution be used care must be taken to avoid excess which dissolves the barium metaborate.

(*b*) Calcium nitrate solution gives a similar precipitate soluble in acetic acid.

4. Silver nitrate solution gives a colourless precipitate of silver metaborate, soluble with ease in dilute nitric acid, and decomposed on heating to give brown silver oxide:

$$2AgNO_3+Na_2B_4O_7+3H_2O = 2AgBO_2+2H_3BO_3+2NaNO_3.$$

5. If a solution of a borate be acidified strongly and placed on turmeric paper, which is then dried, a brown stain develops on the paper. Addition of sodium hydroxide solution turns the stain almost black. (Contrast the ordinary colour change in turmeric with alkali.)

The Metal Acids

All the acids considered hitherto have been formed from elements in the 'B' sub-groups of Mendeléef's Periodic Table, that is, from the non-metals and metalloids on the right-hand side of his table. Many of the metals, particularly those now known as 'transition elements', form anions, and in some cases the free acids can be liberated. The ferrocyanides really belong to this class of acid, but the important oxyacids of the metals (excluding amphoteric hydroxides) are confined to the metals of Groups VA, VIA, and VIIA of the periodic table, e.g. vanadates, chromates, molybdates, tungstates, and permanganates. Of these the CHROMATES and PERMANGANATES are by far the most important and are discussed below.

Chromates and Dichromates

Chromic acid H_2CrO_4 exists in a solution of its anhydride CrO_3. It gives rise to chromates, e.g. potassium chromate K_2CrO_4, and dichromates, e.g. potassium dichromate $K_2Cr_2O_7$ (cf. pyrosulphuric acid $H_2S_2O_7 = H_2SO_4 + SO_3$). The chromate ion CrO_4'' is converted to the dichromate ion Cr_2O_7'' by the addition of hydrogen ions to its solution: $2CrO_4'' + 2H^{\cdot} \rightleftharpoons H_2O + Cr_2O_7''$. The chromate ion gives *yellow* solutions; those containing the dichromate ion are *red-orange*. The outstanding characteristic of these ions is the ease with which they are reduced to give the green chromic ion $Cr^{\cdots}$. This is the basis of the tests described under **Sulphides 8** and **Sulphites 5**. Many other reducing agents effect this change.

SOLUBILITY AND STABILITY. The chromates of the alkali metals and magnesium are readily soluble in water, those of calcium and strontium less so. The remaining normal chromates which have been prepared appear to be insoluble, but they are not always precipitated by potassium chromate solution as hydrolysis often produces basic compounds, and reduction of the chromate ion is also possible (with $Fe^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, &c.). Double salts and dichromates are also formed in some cases. The principal insoluble normal (precipitated) chromates are those of barium, tin, lead, mercury, and silver, whose characteristic colours make them useful in confirmatory tests; basic precipitates are given readily by ferric, aluminium, cupric, and bismuth ions and under certain conditions by cobalt, zinc, and cadmium. The only familiar solid dichromates are those of sodium, potassium, and ammonium, all of which are soluble.

On ignition most chromates are unaffected, although oxygen is readily given to reducing agents. Alkali dichromates are decomposed, giving chromates, chromic oxide Cr_2O_3, and oxygen

$$4K_2Cr_2O_7 = 4K_2CrO_4+2Cr_2O_3+3O_2.$$

Ammonium chromate however gives chromic oxide, ammonia, nitrogen, and water:

$$2(NH_4)_2CrO_4 = Cr_2O_3+2NH_3+N_2+5H_2O,$$

while ammonium dichromate gives chromic oxide, nitrogen, and water only:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3+4H_2O+N_2.$$

Mercurous chromate forms chromic oxide, mercury, and oxygen on decomposition:

$$4Hg_2CrO_4 = 2Cr_2O_3+8Hg+5O_2.$$

Identification

With the dry salts.

1. Apart from the conversion of the yellow chromates to red dichromates, neither dilute hydrochloric acid nor concentrated sulphuric acid shows any visible reaction with these salts. Concentrated sulphuric acid will probably liberate red crystals of chromic anhydride CrO_3. If the salt be warmed with hydrochloric acid some chlorine will be liberated, especially if the acid be concentrated:

$$2K_2CrO_4+16HCl = 2CrCl_3+4KCl+8H_2O+3Cl_2.$$

With solutions.

2. (*a*) Barium nitrate solution gives with a neutral solution of a chromate a pale yellow precipitate of barium chromate $BaCrO_4$, soluble in dilute nitric acid.

(*b*) Calcium nitrate solution gives *no* precipitate with a chromate.

3. With silver nitrate solution a neutral solution of a chromate gives a characteristic terracotta-coloured precipitate of silver chromate soluble in dilute nitric acid. A dichromate may give at first the darker coloured silver dichromate which is decomposed in boiling water to give the normal chromate.

4. An extremely sensitive test for chromates is given by hydrogen peroxide in the presence of acid. An intensely blue solution of *perchromic acid* is formed. The substance is very unstable and rapidly decomposes with loss of oxygen in the presence of excess hydrogen peroxide, leaving a green chromic salt. The blue perchromic acid may be extracted by ether in which it is soluble and comparatively stable. Its constitution is uncertain and anomalous.

5. On boiling a solution of a chromate in dilute hydrochloric acid with alcohol, the *orange* colour of the *dichromate* ion is changed to the *green* colour of the *chromic* ion. At the same time the alcohol is oxidized to *acetaldehyde* which may be recognized by its smell (cf. sulphide and sulphite reductions).

$$H_2Cr_2O_7+6HCl+3C_2H_5OH = 2CrCl_3+7H_2O+3CH_3{\cdot}CHO.$$

Permanganates

These are not 'per-compounds' strictly speaking, as the manganese is exercising a normal group valency of seven in *permanganic acid* $HMnO_4$, and they are not derivatives of hydrogen peroxide. Like the chromates they are characterized by intense colour (purple-red in this case) and vigorous oxidizing action. The free acid is known only in solution.

SOLUBILITY AND STABILITY. All permanganates are appreciably soluble in water. On heating they decompose with evolution of *oxygen*, the corresponding manganate and manganese dioxide being left as residue:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

Identification

With the dry salts.

1. Dilute hydrochloric acid has no reaction with permanganates in the cold, but chlorine is evolved on warming:

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

2. Concentrated sulphuric acid dissolves permanganates converting them into permanganic anhydride Mn_2O_7. The solution has a deep green colour and is liable to explode violently upon a slight rise in temperature. Manganese dioxide is left after the explosion. *This test should be carried out with very small quantities of material.*

$$H_2SO_4 + 2KMnO_4 = Mn_2O_7 + K_2SO_4 + H_2O.$$

With solutions.

3. As all permanganates are soluble they give no characteristic precipitation reactions with cations.

4. A solution of a permanganate acidified with dilute sulphuric acid is reduced to manganous sulphate and potassium sulphate by many reducing agents (e.g. ferrous ions, stannous ions, hydrogen sulphide, sulphurous acid, nitrous acid, oxalates). The permanganate colour disappears during reduction.

$$\begin{aligned}&2KMnO_4 + 10FeSO_4 + 8H_2SO_4\\&\qquad = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.\end{aligned}$$

5. Reduction of a permanganate in alkaline solution gives a green solution of the corresponding manganate; e.g. the reduction of potassium permanganate by aluminium in sodium hydroxide solution.

Reduction of a permanganate in neutral solution gives a brown precipitate of hydrated manganese dioxide.

III

THE ANALYTICAL CHEMISTRY OF THE COMMON CATIONS

The Structure of Cations

A *simple cation* consists of an atom which has given up one or more electrons.

A *complex cation* consists of a group of atoms which have given up one or more electrons. The atoms in the groups may be linked by covalencies or by co-ordination. Whereas the co-ordination in anions is usually donation *from* a central atom (see p. 25) as the negative charge on the ion tends to repel or diffuse electrons, co-ordination in a cation is usually donation *to* a central atom. The principal cationic co-ordinating agents are water and ammonia.

Examples: (*a*) *Simple*: $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$.

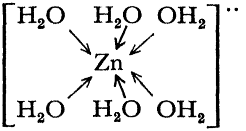
(*b*) *Complex*:

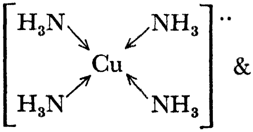
(i) By simple sharing $(NH_4)^{\cdot}$. The nitrogen makes four shared pairs with the four electrons from the hydrogen atoms, and loses its fifth valency electron to the anion on ionization.

$[Hg\text{–}Hg]^{\cdot\cdot}$ the *mercurous* ion: in this case the usual 'octet' of electrons is not completed, nor are all its available valency electrons used by the metal. Two electrons remain in the complex which in this respect (and in its chemistry to some extent) resembles $Pb^{\cdot\cdot}$ which also loses two only out of its four available valency electrons.

(ii) By co-ordination. $[Zn.6H_2O]^{\cdot\cdot}$, $[Cu.4NH_3]^{\cdot\cdot}$, $[Co(NH_3)_6]^{\cdot\cdot\cdot}$,

written





&c.

In the first case the oxygen atoms, having shared two of their six electrons, have still two pairs which can be donated. As a rule only one pair is donated at a time. Nitrogen in ammonia having shared three electrons has a single *lone pair* for co-ordination.

(iii) *By mixed sharing and co-ordination.* $[Co(NH_3)_5Cl]^{\cdot\cdot}$. The cobalt is in the cobaltic state with three valency electrons available, two of which are lost on ionization. The third makes a shared pair with an electron from the chlorine atom, and the other five pairs are *accepted* from the ammonia.

The action of air, oxygen, water, and acids upon metals

The action of water and acids upon metals is a process of oxidation, the ease with which the metals are attacked running roughly parallel to their susceptibility to atmospheric oxidation. The action of the oxygen in the air is usually profoundly modified, however, by the action of water vapour and acid gases.

The oxidation of a metal by an acid can take place in two ways:

(i) *In dilute acids*: by the transference of positive charges from the hydrogen ions present to the metal, with liberation of the discharged hydrogen.

(ii) *In concentrated oxyacids* (e.g. HNO_3, H_2SO_4) where the effective concentration of the hydrogen ions is very small, by the decomposition of the molecule of acid as a whole. The usual products are oxides lower than the anhydride of the acid used (NO_2, NO, SO_2, &c.), but the non-metal elements (N_2, S) and their hydrides (NH_3, H_2S) may be formed. Specific examples are noted below.

Classification of the metals may therefore be made as follows:

(*a*) Metals readily tarnishing (oxidizing) in cold air include SODIUM, POTASSIUM, BARIUM, STRONTIUM, CALCIUM. (These, together with magnesium, constitute the *third main group* in cation analysis.) Very vigorous action ensues with oxygen at higher temperatures, and their oxides are reduced with difficulty. These metals decompose cold water with liberation of hydrogen and formation of a soluble hydroxide:

$$2K + 2H_2O = 2KOH + H_2 \text{ or } 2K + 2H^{\cdot} = 2K^{\cdot} + H_2.$$

The second equation represents the action of dilute acids as well as that of water.

$$2K + 2HCl = 2KCl + H_2 \text{ or } 2K + 2H^{\cdot} = 2K^{\cdot} + H_2.$$

Where cold water reacts with a metal, the action of even dilute acids is usually very violent, the hydrogen often being ignited. With concentrated oxyacids the reaction is so violent that explosions may occur, as with sodium and concentrated nitric acid.

(*b*) Metals which react vigorously with oxygen at high temperatures and form basic oxides reduced with difficulty include MAGNESIUM and ALUMINIUM. More easily reduced oxides are formed by ZINC, CADMIUM, CHROMIUM, and MANGANESE. All these metals attack water (steam) practically irreversibly; that is to say, their normal oxides are not reduced when heated in a stream of hydrogen.

$$Zn + H_2O = ZnO + H_2.$$

(*c*) Metals which oxidize when heated in oxygen and attack steam reversibly (so that their normal oxides are reduced when heated in a stream of hydrogen) include IRON, COBALT, and NICKEL.

With the exception of magnesium and cadmium (*b*) and (*c*) comprise the elements of the *second main group* of cations. Theoretically they should all turn hydrogen out of dilute acids, and should reduce the molecules of concentrated oxyacids. The following points should be noted however. (I) Neither dilute nor concentrated nitric acid attacks *aluminium* at all readily. (ii) Concentrated, or better, fuming, nitric acid may render *iron*, *nickel*, and *chromium* 'passive', that is, insusceptible to attack by dilute acids. (iii) The action of concentrated nitric acid on metals is to give nitrogen peroxide NO_2 (as nitric oxide is itself oxidized by concentrated nitric acid.) (iv) With nitric acid of suitable dilution *magnesium* can give hydrogen and *zinc* can give nitrous oxide and ammonia (as ammonium nitrate), otherwise nitric oxide is the main gaseous reduction product of dilute nitric acid. (v) Dilute and concentrated hydrochloric and dilute sulphuric acid give hydrogen in every case. Cold concentrated sulphuric acid has no action, but on heating it is reduced to sulphur dioxide and in some cases (e.g. with *zinc*) some hydrogen sulphide and free sulphur may be formed.

(*d*) Metals which do not react with water appreciably include COPPER, SILVER, MERCURY, TIN, LEAD, ARSENIC, ANTIMONY, and BISMUTH. With cadmium they constitute the *first main group* in cation analysis. All these metals except *silver* are oxidized by heating in oxygen. Their oxides are reduced completely by heating in hydrogen, and in the case of *silver* and *mercury* the oxides are sufficiently unstable to be decomposed by heat alone. The metals do not react with dilute acids as such, i.e. they are not oxidized at the expense of the positive charges on hydrogen ions. They can, however, reduce the molecules of oxyacids. *Copper*, *silver*, *mercury*, and *bismuth* show no reaction with hydrochloric acid, dilute or concentrated, nor with dilute sulphuric acid. With hot concentrated sulphuric acid, sulphur dioxide is evolved; with dilute nitric acid, nitric oxide is formed, and with concentrated nitric acid, nitrogen peroxide is formed. *Lead* behaves in the same way except that hot concentrated hydrochloric acid will dissolve it slowly. *Antimony* is attacked with readiness by hot concentrated nitric acid only, with formation of the oxides Sb_2O_4 and Sb_2O_5 which are insoluble, and nitrogen peroxide; hot concentrated hydrochloric acid dissolves it very slowly. *Arsenic* is attacked by concentrated nitric or sulphuric acids with formation of arsenic pentoxide As_2O_5 and nitrogen peroxide or sulphur dioxide respectively. *Tin* behaves on the whole like a metal of class (*c*) above, but is extremely slow in its reactions with dilute hydrochloric and sulphuric acids. Concentrated hydrochloric acid gives hydrogen readily; dilute nitric acid can yield ammonium nitrate, but the usual reaction of nitric acid is to yield nitric oxide or nitrogen peroxide according to concentration, and to convert the tin to metastannic acid (hydrated SnO_2).

Characteristic ionic reactions of the cations

For elementary purposes it is impossible to consider the whole chemistry of each cation, but the reactions of each with a few typical anions are usually sufficient for purposes of identification. Thus it is important to know the character of the following compounds of each ion:

(*a*) with anions containing elements in the VIIth periodic group, (i) *chloride*, (ii) *iodide*;

(*b*) with anions containing elements in the VIth periodic group, (iii) *oxide* and (iii*a*) *hydroxide*, (iv) *sulphide*, (v) *sulphate*, (vi) *chromate*;

(*c*) with anions containing elements in the IVth and Vth periodic group, (vii) *carbonate* and (viii) *phosphate*.

The last four anions are generally less important than the rest. The usual reagents for the production of these compounds are: (i) *dilute hydrochloric acid*, (ii) *potassium iodide*, (iii) and (iii*a*) *sodium* (or *potassium*) *hydroxide* and *ammonium hydroxide*, (iv) *hydrogen sulphide*, (v) *sulphuric acid*, (vi) *potassium chromate*, (vii) *ammonium carbonate* $(NH_4)_2CO_3$, (viii) *sodium hydrogen phosphate* Na_2HPO_4.

These cover most of the tests carried out in analysis for cations, but there are nearly always one or two special tests for each ion which throw considerable light on the chemistry of the element concerned. It should be noted how the group reagents give results in accord with the periodic classification as illustrated by **Tables I, II, IIA, III**, and **IIIA** (pp. 219–221).

In some cases it is unnecessary to use more than two or three of the reagents mentioned, but qualitative analysis becomes a more rational proceeding if the more complete behaviour of an ion is kept in mind. Non-ionic reactions of solid compounds ('dry tests') are discussed on pp. 132–138. Those giving positive results are indicated at the end of the ionic reactions for each cation concerned. For convenience in reference and discussion, the reactions of cations usually included in elementary systems of analysis are described below in the order of the analytical groups.

The First Main Group

The First Main Group includes the cations formed by SILVER, MERCURY, LEAD, COPPER, CADMIUM, BISMUTH, ANTIMONY, ARSENIC, and TIN, all of which form sulphides insoluble in 0·25 *N* hydrochloric acid (mercurous sulphide does not exist, being decomposed on formation into mercury and mercuric sulphide). The position in the Periodic Table of the complete group of sulphides 'insoluble in acid' is given in **Table IIA** (p. 220). The group contains a sub-group of cations forming insoluble or sparingly soluble chlorides. These include the silver, mercurous, lead, and cuprous ions. The instability of the cuprous ion in solution makes it relatively unimportant analytically The periodic relations of the chloride sub-group are shown in **Table I** (p. 219). The reason for its consideration as part of the sulphide group is given on p. 17.

Silver

Normal oxide Ag_2O: dark brown or black, readily decomposed; peroxide Ag_2O_2: black, very unstable.

The silver ion is monovalent and colourless. In the solid state the following compounds are coloured: *bromide* (cream), *iodide* (yellow), *sulphide* (black), *phosphate* (yellow), *arsenite* (yellow), *arsenate* (brown), *ferricyanide* (orange), *chromate* (terra-cotta), *permanganate* (almost black). Most of the salts darken in colour when exposed to light. For the solubility of silver salts, compare the precipitation of these salts as characteristic of the anions. The nitrate, chlorate, perchlorate, permanganate, fluoride, and sulphate are soluble in water, the acetate and nitrite are sparingly soluble. The hypochlorite breaks up into the soluble chlorate and insoluble chloride; all other inorganic silver salts are insoluble in water.

PRINCIPAL REACTIONS (*use a solution of silver nitrate*).

1. Dilute hydrochloric acid added to a soluble silver salt gives a white precipitate of silver chloride $AgCl$, insoluble in acids, which gradually darkens in sunlight. The precipitate is insoluble in hot water, but is soluble in ammonium hydroxide solution, as the chloride and hydroxide of the complex cation formed are soluble and insufficient silver ion is left in solution to form a precipitate with the chloride ion or hydroxide:

$$AgCl+2NH_4OH \rightleftharpoons [Ag(NH_3)_2]Cl+2H_2O.$$

2. Potassium iodide solution gives a pale yellow precipitate of silver iodide AgI, insoluble in ammonium hydroxide.

3. Sodium hydroxide solution precipitates brown *silver oxide* Ag_2O which is insoluble in excess of the precipitant:

$$2AgNO_3+2NaOH = 2NaNO_3+Ag_2O+H_2O.$$

4. Ammonium hydroxide solution gives a similar precipitate (colourless at first) which readily dissolves in excess ammonium hydroxide (see **7** below).

5. Hydrogen sulphide gives a black precipitate of silver sulphide Ag_2S which is insoluble in alkali sulphide (cf. Ag_2O), but which is dissolved slowly by hot dilute nitric acid owing to its oxidation to silver sulphate which is moderately soluble.

6. Potassium chromate solution gives a terracotta-coloured precipitate of silver chromate Ag_2CrO_4, soluble in dilute nitric acid.

For the precipitation of other silver salts, see under the appropriate anions.

SPECIAL REACTIONS: (*a*) *Complex ion formation.*

7. The solubility in ammonium hydroxide solution of many insoluble silver salts is due to formation of the complex cation $[Ag(NH_3)_2]^{\cdot}$. The formation of this ion removes silver ions from solution until the solubility product of, say, silver chloride is no longer exceeded. The number of silver ions produced by dissociation of the complex is sufficient, however, to precipitate the much less soluble silver iodide.

The following reactions illustrate the formation of complex anions which are so little dissociated that the concentration of silver ion in equilibrium with them even in dilute solution is insufficient to exceed the solubility product of most of the insoluble silver salts.

7*a*. Potassium cyanide solution added to a solution of a silver salt precipitates colourless silver cyanide, which is soluble in excess of the potassium cyanide solution:

$$AgCN + CN' = [Ag(CN)_2]'.$$

7*b*. Sodium thiosulphate solution precipitates and redissolves in a similar manner silver thiosulphate:

$$Ag_2S_2O_3 + Na_2S_2O_3 = 2Na[AgS_2O_3].$$

Insoluble silver salts, except the extremely insoluble silver sulphide, are therefore readily soluble in potassium cyanide or sodium thiosulphate solution. The reaction **7*a*** is used to maintain a supply of silver ions at low concentration for silver plating, and **7*b*** for dissolving unaffected silver halides in fixing a photographic plate.

(*b*) *Ease of reduction.*

8. If to a solution of a silver salt in a clean test-tube ammonium hydroxide be added until the brown precipitate of silver oxide first formed is just redissolved, and then a few drops of a soluble tartrate added and the whole gently warmed, a mirror of metallic silver is deposited on the walls of the test-tube.

DRY TEST

Heated with alkali carbonate on charcoal silver salts give a malleable bead of silver with no incrustation of oxide.

Lead

The normal oxide for salts is the monoxide PbO 'litharge' which may be yellow or orange in colour and is stable to heat, although it may take up oxygen. There are two *intermediate* oxides Pb_2O_3 (orange red) and Pb_3O_4 'minium' or 'red lead' (bright red) and a chocolate-brown *dioxide* PbO_2. These yield oxygen on heating and oxidize hydrochloric acid to chlorine. Nitric acid attacks the intermediate oxides forming lead nitrate and leaving a residue of the dioxide which it does not dissolve.

The lead ion is divalent and colourless. The *iodide* (yellow), *sulphide* (black), and *chromate* (yellow) are the only common salts of lead which are coloured in the solid state. Lead salts are insoluble or sparingly soluble in water with the exception of the *nitrate* and *acetate*; they are, however, soluble in nitric acid.

PRINCIPAL REACTIONS (*use a solution of lead nitrate*).

1. Dilute hydrochloric acid added to a moderately concentrated solution of a lead salt precipitates white lead chloride $PbCl_2$. The precipitate is soluble in hot water, and in concentrated hydrochloric acid in which it forms a complex anion:

$$PbCl_2+HCl = H(PbCl_3).$$

2. Potassium iodide solution gives a bright yellow precipitate of lead iodide PbI_2 which can be recrystallized from its *colourless* solution in hot water as glistening hexagonal plates.

3. Sodium hydroxide solution precipitates white lead hydroxide $Pb(OH)_2$ which is soluble in excess of the precipitant to form sodium plumbite. This solution is used in detecting traces of hydrogen sulphide, as the alkalinity favours the formation of sulphide ion, while the plumbite is sufficiently dissociated to give the requisite lead ions.

$$Pb(OH)_2+2NaOH \rightleftharpoons Na_2PbO_2+2H_2O$$

$$H_2S+Na_2PbO_2 = PbS+2NaOH;$$

cf. **Sulphides 3.**

Ammonium hydroxide solution will precipitate but will not redissolve lead hydroxide.

4. Hydrogen sulphide precipitates black lead sulphide PbS from solutions of lead salts. A red chlorosulphide is sometimes formed. Lead sulphide is insoluble in alkali sulphide, but soluble in hot dilute nitric acid and in concentrated hydrochloric acid. It is converted by treatment with hydrogen peroxide into white insoluble lead sulphate:

$$PbS+4H_2O_2 = PbSO_4+4H_2O.$$

5. Dilute sulphuric acid gives a white precipitate of lead sulphate with lead salts. The precipitate will dissolve in concentrated solutions of ammonium acetate owing to the comparatively low ionization of lead acetate.

6. Potassium chromate solution gives a yellow precipitate of lead chromate $PbCrO_4$ ('chrome yellow') which is converted to a red basic salt $Pb_2\,[CrO_4(OH)_2]$ ('chrome red') on heating with lime:

$$2PbCrO_4+Ca(OH)_2 = Pb_2[CrO_4(OH)_2]+CaCrO_4.$$

7. Ammonium carbonate solution gives a white precipitate of basic lead carbonate ('white lead').

DRY TESTS

Heated with alkali carbonate on charcoal lead salts give a malleable bead of lead with a yellow oxide incrustation.

Flame: bluish-white (not conclusive).

Mercury

37

Oxides: mercurous oxide Hg_2O (black) and mercuric oxide HgO (red or yellow) both readily decomposed by heat. The **mercurous** ion consists of two atoms linked non-ionically (see p. 77) and carrying a total positive charge of two electronic units. Most of the mercurous salts are very little ionized and are often decomposed with ease into mercury and the corresponding mercuric salt: $Hg_2^{\cdot\cdot} = Hg + Hg^{\cdot\cdot}$. They are salts of a weak base and show hydrolysis (formation of basic salts); the *nitrate*, *fluoride*, and *chlorate* are soluble in water and a few others are sparingly soluble. The ion is colourless in solution. The solid *iodide* is green, the *chromate* red, the *fluoride* and *nitrite* yellow.

PRINCIPAL REACTIONS OF THE MERCUROUS ION (*use a solution of mercurous nitrate*).

1. Dilute hydrochloric acid added to a solution of a mercurous salt gives a white precipitate of mercurous chloride ('calomel') Hg_2Cl_2. The precipitate is insoluble in hot water, and is blackened by ammonium hydroxide solution, owing to the separation of mercury and the formation of *mercuric-ammonia* complexes (see **Mercuric ion 3**).

2. Potassium iodide solution gives a dull green precipitate of mercurous iodide Hg_2I_2, considered by some chemists to be an intimate mixture of mercury and mercuric iodide into which it eventually separates. The mercuric iodide dissolves in excess of the potassium iodide solution.

3. Sodium hydroxide solution gives a black precipitate of mercurous oxide Hg_2O insoluble in excess of the precipitant:

$$2NaOH + Hg_2(NO_3)_2 = 2NaNO_3 + Hg_2O + H_2O.$$

4. Ammonium hydroxide solution reacts with mercurous compounds but the resulting product is a mixture of a mercuric compound and metallic mercury, which, owing to its fine state of division, appears black.

The constitution of the remainder depends upon the conditions and the mercurous salt used. It is usually in the form of a basic salt with co-ordinated ammonia. The most important case is the reaction of ammonium hydroxide with mercurous chloride described above.

5. Hydrogen sulphide gives a black precipitate consisting of a mixture of mercury and mercuric sulphide. Mercuric sulphide is so very insoluble that it removes practically all mercuric ions from solution and the equilibrium $Hg_2^{\cdot\cdot} \rightleftharpoons Hg + Hg^{\cdot\cdot}$ is consequently displaced entirely in favour of the mercuric compound (cf. the non-existence of mercurous cyanide and instability of mercurous iodide).

6. Sulphuric acid gives a white precipitate of mercurous sulphate.

7. Potassium chromate gives a brick-red precipitate of mercurous chromate.

Mercurous carbonate does not exist; the phosphate is easily decomposed.

The **mercuric** ion is also colourless, although as usual the solid *iodide*, *sulphide*, and *chromate* show characteristic colours (see below). Many of the salts are very weak electrolytes and do not give complete ionic reactions. *Mercuric cyanide* is a moderately soluble non-electrolyte, but reacts with potassium iodide (see **1**). The salts are readily hydrolysed in solution. Several of them show a slight solubility in water, the chloride and nitrate being the most important of those which are readily soluble.

PRINCIPAL REACTIONS OF THE MERCURIC ION (*use a solution of mercuric nitrate*).

1. Mercuric chloride, is soluble, but potassium iodide solution gives with solutions of mercuric salts a bright red precipitate (pink at first) of mercuric iodide HgI_2, soluble in excess of the precipitant:

$$2KI + HgI_2 = K_2(HgI_4).$$

The stability of the complex may be judged from the fact that no mercuric oxide is precipitated from this solution by caustic alkali; the alkaline solution of the complex is in fact used as a test for ammonia in 'Nessler's reagent'. (see **Ammonium 2**).

Red mercuric iodide turns yellow on heating, the change being reversed when the cold yellow form is scratched.

2. Sodium hydroxide solution precipitates yellow mercuric oxide insoluble in excess of the alkali:

$$2NaOH+HgCl_2 = 2NaCl+HgO+H_2O.$$

3. Ammonium hydroxide solution forms with mercuric chloride the compound known as 'infusible white precipitate' with the formula $Hg(NH_2)Cl$:

$$HgCl_2+2NH_4OH = NH_4Cl+Hg(NH_2)Cl+2H_2O.$$

In other cases basic 'amino' derivatives are formed.

4. From a solution of a mercuric salt acidified with dilute hydrochloric acid, hydrogen sulphide precipitates eventually mercuric sulphide which is black. The initial precipitate is a *white chlorosulphide* $Hg_3Cl_2S_2$ which changes colour through yellow and brown to black.

Mercuric sulphide also occurs in a red form, *vermilion* or *cinnabar*. It is insoluble in ammonium polysulphide, and in hot dilute nitric acid.

5. Sulphuric acid gives no precipitate with mercuric salts, but potassium chromate solution gives a yellow precipitate of mercuric chromate, $HgCrO_4$. The phosphate is also insoluble, and the carbonate does not exist.

SPECIAL REACTIONS

6. *Reduction*: stannous chloride solution reduces a mercuric salt first to insoluble mercurous chloride (white) and then to metallic mercury (grey-black):

$$2HgCl_2+SnCl_2 = SnCl_4+Hg_2Cl_2$$

$$Hg_2Cl_2+SnCl_2 = SnCl_4+2Hg.$$

DRY TESTS

Mercury compounds generally sublime on heating, sometimes with decomposition. When they are heated with sodium carbonate in a test-tube fine drops of mercury (which will coalesce on rubbing) condense on the walls of the tube. When heated with carbonate on charcoal there is no obvious result, as the mercury formed volatilizes away and leaves no oxide.

Bismuth

The normal oxide for salts is the yellow Bi_2O_3. Two brown oxides Bi_2O_4 and Bi_2O_5 are formed which give up oxygen on heating and can be used as moderately strong oxidizing agents on this account. Bi_2O_5 shows weak acid properties. The bismuth ion is trivalent and colourless. It reacts with water, hence all soluble bismuth salts are converted by water into insoluble compounds of a basic character; these are soluble in excess acid, the hydrogen ion of the acid displacing the equilibrium in favour of the bismuth ion.

$$Bi^{\cdot\cdot\cdot} + H_2O \rightleftharpoons BiO^{\cdot} + 2H^{\cdot}.$$

Of the solid compounds of bismuth the *sulphide* is brown and the *iodide* black.

PRINCIPAL REACTIONS (*use a solution of bismuth nitrate in just enough nitric acid to keep it clear*).

1. (*a*) Bismuth chloride is soluble, but the chloride of the ion $BiO^{\cdot}$ is insoluble (see **6** below).

(*b*) Potassium iodide precipitates black bismuth iodide BiI_3 which redissolves in excess potassium iodide to give a yellow solution:

$$BiI_3 + KI = K(BiI_4).$$

The complex is decomposed on dilution, giving first the black iodide, and then the orange basic iodide (BiO)I.

2. Sodium hydroxide solution precipitates white bismuth hydroxide $Bi(OH)_3$ which is partially dehydrated on heating and turns yellow in consequence.

3. Ammonium hydroxide solution precipitates from solutions of bismuth salts corresponding basic salts, though these are not always constant in composition. The precipitates formed are colourless and insoluble in excess of ammonium hydroxide solution.

4. Hydrogen sulphide added to a solution of a bismuth salt acidified with dilute hydrochloric acid gives a brown precipitate of bismuth sulphide, Bi_2S_3, insoluble in ammonium polysulphide, but soluble in hot dilute nitric acid.

5. Basic salts are precipitated by dilute sulphuric acid, potassium chromate and ammonium carbonate: the normal phosphate is precipitated by sodium phosphate.

SPECIAL REACTIONS

6. A solution of a bismuth salt poured into a large quantity of water gives a white precipitate of the corresponding basic salt, e.g.

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

$$2Bi(NO_3)_3 + 3H_2O = Bi_2O_2(OH)(NO_3) + 5HNO_3.$$

7. *Reduction.* Solutions of bismuth salts are reduced to a black precipitate of metallic bismuth when treated with alkali stannite (stannous hydroxide dissolved in sodium hydroxide solution):

$$\begin{aligned}&2Bi(NO_3)_3 + 3Na_2SnO_2 + 6NaOH \\ &\qquad = 2Bi + 6NaNO_3 + 3Na_2SnO_3 + 3H_2O.\end{aligned}$$

DRY TEST

Heated with alkali carbonate on charcoal bismuth compounds give a brittle bead of the metal with a yellow incrustation of oxide.

Copper

Copper forms two oxides; dark red **cuprous** oxide Cu_2O and black **cupric** oxide CuO. Both oxides are fairly stable to heat but lose oxygen at very high temperatures. Each gives rise to a set of salts. The equilibrium in solution between the cations of these salts,

$$2Cu^{\cdot} \rightleftharpoons Cu^{\cdot\cdot}+Cu,$$

is almost completely in favour of the right-hand, or *cupric* side of the equation. In the presence of water, therefore, cuprous compounds can be prepared only if (i) they are insoluble, or (ii) they are stabilized in solution by forming complex ions, e.g. with concentrated hydrochloric acid. Removal of cuprous ions results in both cases. The cuprous ion itself is probably colourless, while the hydrated cupric ion is blue.

In *dilute* acid solution the copper is invariably present as *cupric* ions and it is the solutions of these ions that are of account in analysis. It should be noted that cupric cyanide and cupric iodide have *not* been isolated, the cuprous derivatives being stable (and insoluble) in these two cases. The cupric salts have in most cases solubilities characteristic of the salts of a heavy metal. The reactions given below are those of the cupric ion, but a few reactions of copper in the cuprous condition are added for comparison.

PRINCIPAL REACTIONS (*use a solution of copper sulphate*).

1. (*a*) Cupric chloride is soluble.

(*b*) Potassium iodide solution added to a solution of a cupric salt precipitates white cuprous iodide and liberates iodine, which dissolves in excess of the potassium iodide solution (and can be removed by sodium thiosulphate solution):

$$4KI+2CuSO_4 = 2K_2SO_4+2CuI+I_2.$$

2. Sodium hydroxide solution precipitates blue cupric hydroxide $Cu(OH)_2$ insoluble in excess alkali, and which decomposes on heating to give black cupric oxide CuO.

3. Ammonium hydroxide solution precipitates a pale blue basic salt, which readily redissolves in excess of the precipitant to give a characteristic deep blue solution containing the tetrammine cupric ion:

$$Cu^{\cdot\cdot}+4NH_3 = [Cu(NH_3)_4]^{\cdot\cdot}.$$

4. Hydrogen sulphide added to a solution of a cupric salt acidified with dilute hydrochloric acid precipitates black cupric sulphide CuS, which is very slightly soluble in ammonium polysulphide, and readily soluble in hot dilute nitric acid.

5. Cupric sulphate is soluble, but the phosphate and carbonate are insoluble. A soluble dichromate exists but a basic chromate is precipitated by potassium chromate.

Special Reactions

6. Potassium ferrocyanide solution produces a brown precipitate of cupric ferrocyanide $Cu_2[Fe(CN)_6]$.

7. On boiling a faintly acid solution of a copper salt with a concentrated solution of sodium thiosulphate, a black precipitate of *cuprous sulphide* Cu_2S is formed. Sulphur is also deposited.

The cupric thiosulphate is soluble in the excess of sodium thiosulphate solution but breaks up to form the corresponding complex of the cuprous ion, sulphur and free sulphuric acid being formed simultaneously. The cuprous complex breaks up on boiling to form cuprous sulphide and sulphuric acid. In these reactions is seen the similarity of monovalent copper to silver (see **Thiosulphates 3**).

$$CuS_2O_3+Na_2S_2O_3 = Na_2[Cu(S_2O_3)_2]$$
$$2Na_2[Cu(S_2O_3)_2]+H_2O = 2Na(CuS_2O_3)+Na_2S_2O_3+S+H_2SO_4$$
$$2Na(CuS_2O_3)+H_2O = Na_2S_2O_3+Cu_2S+H_2SO_4.$$

8. Potassium cyanide solution precipitates cupric cyanide which is immediately decomposed to white *cuprous cyanide* CuCN and cyanogen. The cuprous cyanide dissolves in excess potassium cyanide forming a solution of potassium cuprocyanide, in which the concentration of cupric or cuprous ions is so low that it is insufficient to give a precipitate with hydrogen sulphide.

REACTIONS OF THE CUPROUS COMPOUNDS

9. From a solution of cuprous chloride in concentrated hydrochloric acid (which can be prepared by reducing a cupric chloride solution with copper or sulphurous acid) the insoluble *iodide* (white), *hydroxide* (yellow—changing to red on dehydration), *sulphide* (black), and *cyanide* (white, soluble in excess potassium cyanide solution) can be precipitated by the appropriate reagents.

DRY TESTS

Heated with alkali carbonate on charcoal copper compounds give a malleable bead of metal or a finely divided metallic powder, with no oxide visible.

Borax bead: green (hot) and blue (cold) in the oxidizing flame, red in the reducing flame.

Flame: green (especially in the presence of halides).

Cadmium

The normal oxide for cadmium salts is CdO (brown) but a black suboxide Cd_2O probably exists. The ion is divalent and colourless. The sulphide is yellow in the solid state. There is nothing abnormal in the solubilities of cadmium salts. The chloride and the iodide are both soluble.

PRINCIPAL REACTIONS (*use a solution of cadmium nitrate*).

1. Sodium hydroxide solution precipitates white cadmium hydroxide $Cd(OH)_2$ which does not redissolve in excess of the precipitant (as, unlike its analogue zinc hydroxide, it is *not* ‘amphoteric’). On heating the precipitate it darkens with the formation of the brown oxide CdO.

2. Ammonium hydroxide solution precipitates cadmium hydroxide, which is soluble in excess of the precipitant owing to the formation of a tetrammine cadmium ion.

$$Cd^{\cdot\cdot}+4NH_3 = [Cd(NH_3)_4]^{\cdot\cdot}.$$

3. Hydrogen sulphide added to a solution of a cadmium salt acidified with a *little* dilute hydrochloric acid precipitates finely divided yellow cadmium sulphide CdS. This is insoluble in ammonium polysulphide, but soluble in hot dilute nitric acid and in moderately concentrated hydrochloric acid.

4. Cadmium sulphate is soluble, and the phosphate insoluble in water, while ammonium carbonate solution precipitates basic cadmium carbonate. The normal chromate is insoluble, but is not precipitated by potassium chromate.

Special Reaction

5. Potassium cyanide solution precipitates white cadmium cyanide $Cd(CN)_2$ which is soluble in excess of the precipitant without valency change (contrast copper). There is sufficient cadmium ion present for the precipitation of yellow cadmium sulphide by the action of hydrogen sulphide.

Dry Test

When heated with alkali carbonate on charcoal cadmium compounds give a brown incrustation of cadmium oxide.

Tin

Tin forms two oxides, stannous oxide SnO, which is black, and stannic oxide SnO_2, which is white, the latter being a very stable and refractory substance, while both are associated with amphoteric hydroxides. They give rise to the **stannous** and **stannic** salts respectively; the stannous ion being divalent and the stannic ion tetravalent. Both ions are colourless and both react with water, hence insoluble basic salts tend to separate from solutions containing these ions unless excess acid is present. The *stannic halides* (except SnF_4) are non-electrolytes in the fused state (the chloride is liquid at ordinary temperatures). The solid *iodides* are coloured orange, *stannous sulphide* is brown, and *stannic sulphide* yellow. Other compounds of tin are normally colourless.

Principal Reactions of the Stannous Ion (*use a solution of stannous chloride in dilute hydrochloric acid*).

1. Stannous iodide is sparingly soluble in water and readily soluble in solutions of alkali halides. It is not used therefore in precipitation tests.

2. Sodium hydroxide solution precipitates white stannous hydroxide, soluble in excess of the alkali (*amphoteric hydroxide*). The solution contains sodium stannite.

$$Sn(OH)_2+2NaOH = Na_2SnO_2+2H_2O.$$

Ammonium hydroxide precipitates stannous hydroxide but does not appreciably redissolve it. The precipitated hydroxide will in each case decompose on heating, yielding black stannous oxide.

3. Hydrogen sulphide added to a solution of a stannous salt acidified with hydrochloric acid precipitates brown stannous sulphide SnS, which is soluble in ammonium polysulphide solution and in hot dilute nitric acid.

Stannous sulphide is not sufficiently acidic in character to form a thiostannite by dissolving in normal ammonium sulphide, but the excess sulphur in the polysulphide oxidizes it to the more acidic stannic sulphide which can dissolve to form a thiostannate (cf. **stannic ion 3**).

$$SnS+(NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Note that increase in valency in a metal tends to confer acidic properties: cf. $Mn^{\cdot\cdot}$, $(MnO_4)'$; $Cr^{\cdot\cdot\cdot}$, $[CrO_4]''$; &c.

4. Stannous sulphate is soluble; potassium chromate is reduced to the chromic condition by a stannous salt in the presence of acid; stannous phosphate is insoluble and stannous carbonate does not exist. Ammonium carbonate solution precipitates stannous hydroxide from solutions containing stannous ions.

SPECIAL REACTION

5. Mercuric chloride solution gives a white precipitate of *mercurous chloride* which turns grey with separation of mercury in a fine state of division (see **Mercuric ion 6**).

PRINCIPAL REACTIONS OF THE STANNIC ION

1. Stannic iodide like stannic chloride is hydrolysed by water, and is therefore not precipitated from solution.

2. Sodium hydroxide solution gives with stannic compounds a white gelatinous precipitate of hydrated stannic oxide which redissolves in excess of the alkali to form sodium stannate:

$$Sn(OH)_4+2NaOH = Na_2SnO_3+3H_2O.$$

Ammonium hydroxide precipitates but does not redissolve hydrated stannic oxide.

The oxidation of tin by nitric acid results in the formation of another form of hydrated stannic oxide called *metastannic acid* $(H_2SnO_3)_n$; for differences in the behaviour of these two forms larger texts must be consulted.

3. When added to a solution of a stannic compound, acidified with dilute hydrochloric acid, hydrogen sulphide precipitates yellow stannic sulphide SnS_2 which is soluble in ammonium polysulphide (forming ammonium thiostannate) and in hot dilute nitric acid.

4. Stannic sulphate is soluble but is slowly hydrolysed, with separation of basic salts; yellow stannic chromate can be precipitated in neutral solution only; alkali carbonates precipitate the hydrated oxide.

SPECIAL REACTION

5. Although the formation of 'stannic phosphate' is not used as a test for tin, it is sometimes used for the removal of phosphoric acid in analysis. If metallic tin be added to a solution of a phosphate in nitric acid and the solution boiled, the metastannic acid formed carries with it the free phosphoric acid. It is unlikely that the precipitate contains a genuine *stannic phosphate*.

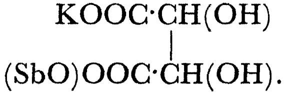
DRY TESTS

When heated with alkali carbonate on charcoal, tin compounds give a malleable bead of tin with no oxide.

Flame: bluish white (not conclusive).

Antimony

The normal oxide for antimony salts is Sb_4O_6 (white); an inert intermediate oxide Sb_2O_4 (white) and an acidic oxide Sb_2O_5 (pale yellow) also exist. The normal oxide also shows weak acid character. The antimony cation is trivalent and colourless; it reacts with water in a manner rather similar to that of the bismuth ion (q.v.), and some of the more familiar compounds of antimony are therefore derivatives of the *antimonyl* ion $SbO^{\cdot}$ rather than of the simple metallic ion, e.g. 'tartar emetic' is *potassium antimonyl tartrate*,



$$\begin{array}{c} KOOC{\cdot}CH(OH) \\ | \\ (SbO)OOC{\cdot}CH(OH). \end{array}$$

It is clear from the equation $Sb^{\cdot\cdot\cdot}+H_2O \rightleftharpoons SbO^{\cdot}+2H^{\cdot}$ that excess acid will repress the hydrolysis of antimony compounds in solution. Most antimony compounds are colourless but the solid *sulphides* are orange. The *antimonates*, derived from pentavalent antimony, are generally similar in behaviour to the arsenates (q.v.) but the insoluble sodium hydrogen pyroantimonate should be noted in particular (**Sodium 1**).

PRINCIPAL REACTIONS (*use a solution of antimony chloride in the minimum quantity of hydrochloric acid necessary to keep the solution clear*).

1. Antimony chloride is soluble in water, but is hydrolysed. On pouring a solution of the chloride into a relatively large quantity of water a fine, heavy, white precipitate of antimony chloride is formed. Further hydrolysis gives the hydrated oxide $Sb_4O_6.xH_2O$ (cf. **Bismuth 6**).

2. Potassium iodide solution gives a yellow coloration with antimony compounds owing to the formation of a complex anion containing antimony and iodine (cf. **Bismuth 1*b***).

3. Solutions of sodium or ammonium hydroxide precipitate the hydrated oxide, which is soluble in concentrated alkali forming antimonites.

4. Hydrogen sulphide added to a solution of an antimonous compound acidified with dilute hydrochloric acid gives an orange precipitate of antimony sulphide Sb_2S_3. The action is easily reversed, i.e. the sulphide dissolves with evolution of hydrogen sulphide, in moderately high concentrations of the acid. The sulphide is soluble in ammonium polysulphide forming ammonium thioantimonate (amphoteric character), and also in hot nitric acid

$$Sb_2S_3+(3(NH_4)_2S+2S) = 2(NH_4)_3SbS_4.$$

The orange pentasulphide Sb_2S_5 is precipitated from a thioantimonate solution by hydrochloric acid.

5. The carbonate is non-existent, ammonium carbonate solution precipitating the hydrated oxide, and in acid sclution potassium dichromate is reduced by *antimonous* compounds.

SPECIAL REACTION

6. On adding sodium thiosulphate solution and warming, red antimony oxysulphide is precipitated:

$$2SbCl_3+3Na_2S_2O_3 = 6NaCl+4SO_2+Sb_2S_2O.$$

Antimonic compounds

Apart from the antimonates, compounds of pentavalent antimony are represented by solutions of the pentoxide in concentrated acids. In this condition their behaviour is parallel to that of the antimonous compounds. Water hydrolyses the chloride with formation of an oxychloride SbO_2Cl, and finally of antimonic acid H_3SbO_4. With acidified potassium iodide solution, however, iodine is liberated (contrast $Sb^{\cdots}$); alkali hydroxides and carbonates precipitate the pentoxide; hydrogen sulphide gives an orange precipitate, in this case the pentasulphide Sb_2S_5, which is soluble in alkali sulphide solutions giving thioantimonates.

DRY TESTS

When heated with alkali carbonate on charcoal antimony compounds give a brittle bead of the metal with a white incrustation of oxide.

Flame: bluish white (not conclusive).

Arsenic

Arsenic forms a 'trioxide' As_4O_6 showing basic and acidic properties, and an acidic pentoxide As_2O_5. Both are white solids, the pentoxide fusing and losing oxygen at high temperatures to form the lower oxide which is volatile and sublimes. These oxides give rise to arsenites and arsenates, the behaviour of which is discussed in Chapter II. The only simple cation formed by arsenic is the trivalent ion $As^{\cdots}$ which is colourless, although the solid sulphide is yellow. It is not a constituent of many isolable compounds but can exist in solution in equilibrium with all compounds of trivalent arsenic.

PRINCIPAL REACTIONS (*use a solution of arsenic chloride: this can be prepared by dissolving arsenic trioxide in dilute hydrochloric acid*).

1. The chloride and iodide are hydrolysed in solution and the products of hydrolysis are soluble. No precipitate is formed therefore with potassium iodide.

2. From dilute solutions of arsenious compounds no hydroxide is precipitated by the addition of either sodium or ammonium hydroxide solutions. (The oxide is sparingly soluble in water and readily soluble in acid or alkali.)

3. Hydrogen sulphide added to a solution of an arsenious compound acidified with dilute hydrochloric acid gives a yellow precipitate of arsenious sulphide As_2S_3. The precipitate is soluble in ammonium polysulphide forming ammonium thioarsenate, and in hot dilute nitric acid.

$$As_2S_3+(3(NH_4)_2S+2S) = 2(NH_4)_3AsS_4.$$

Arsenic pentasulphide As_2S_5 is precipitated from ammonium thioarsenate solution by hydrochloric acid.

If the arsenic is in the pentavalent condition, e.g. as arsenate, precipitation by hydrogen sulphide in acid is preceded by *slow* reduction to the arsenious state. The resulting precipitate is very finely divided and is mixed with colloidal sulphur.

$$2H_3AsO_4+5H_2S = As_2S_3+8H_2O+2S.$$

4. Arsenic does not form solid salts with oxyacids.

SPECIAL REACTIONS

5. *Reducing power of arsenious compounds*: If to a solution of an arsenious salt acidified with dilute hydrochloric acid (essentially a solution of arsenious acid) a few drops of copper sulphate solution be added, and the mixture carefully neutralized by the addition of potassium hydroxide solution, a green precipitate of copper hydrogen arsenite $CuHAsO_3$ is formed (cf. **Arsenites 4**). The precipitate dissolves in excess alkali forming a blue solution which gives on boiling a red precipitate of cuprous oxide.

6. *Reduction of arsenious compounds:* If a saturated solution of stannous chloride be added to an arsenious compound in *concentrated* hydrochloric acid the solution becomes dark brown and finally black, with separation of metallic arsenic. This does not occur in more dilute solutions as it is a reduction of the positive arsenic ions and not of arsenious acid.

$$2AsCl_3+3SnCl_2 = 3SnCl_4+2As.$$

7. Of the tests involving *arsine* AsH_3, the simplest is that due to Gutzeit. If an arsenic compound (use very little) be placed in sulphuric acid in a test-tube and granulated zinc added, arsine is generated along with the hydrogen formed. If a crystal of silver nitrate (or a concentrated solution) be held on a filter paper over the mouth of the tube it is turned first yellow and then black. The yellow compound contains silver arsenide and silver nitrate. Th black substance is metallic silver.

$$AsH_3+6AgNO_3 = 3AgNO_3.AsAg_3+3HNO_3$$
$$AsAg_3.3AgNO_3+3H_2O = H_3AsO_3+6Ag+3HNO_3.$$

DRY TESTS

Arsenic trioxide sublimes readily, and many arsenic compounds give a sublimate on heating.

Heated with alkali carbonate on charcoal they give an incrustation of white arsenic oxide and a smell of garlic when hot.

The First Main Group: Summary

The properties of the characteristic compounds of the elements in this group may be summarized as follows:

Chlorides: Silver, cuprous, and mercurous chlorides are insoluble. Lead chloride is very sparingly soluble in the cold. Other chlorides of the group are soluble. Antimony, bismuth, stannous, stannic, and arsenic chlorides are hydrolysed, antimony, bismuth, and the stannous compounds forming insoluble oxychlorides.

Iodides: Silver, cuprous, mercurous (unstable), mercuric, lead, stannous, and bismuth iodides are insoluble in cold water. Cadmium iodide is soluble; arsenic, antimony, and stannic iodides are hydrolysed by water and are therefore not precipitated by potassium iodide. Some of these iodides form soluble complexes in excess of potassium iodide. Cupric iodide does not exist.

Hydroxides and hydrated oxides: All are insoluble in water except the amphoteric arsenious acid. Those of silver and mercury are very unstable, losing water in the cold. Hydroxides of tin, lead, arsenic, and to a small extent antimony are soluble in sodium hydroxide solution (amphoteric character). Silver, cuprous, cupric, and cadmium hydroxides are soluble in excess of ammonium hydroxide solution, complex ions being formed.

Sulphides: These are all insoluble in water and in 0·25 N acid. Arsenic, antimony, and stannic sulphide are soluble in ammonium sulphide. Stannous sulphide dissolves in ammonium polysulphide. All except mercuric sulphide are soluble in hot, moderately concentrated nitric acid. Mercurous sulphide does not exist.

Sulphates: The sulphates of lead and the mercurous ion are insoluble. Other normal sulphates in the group are soluble, but there are insoluble basic sulphates of bismuth, mercury, tin, and antimony. Arsenic does not form a sulphate.

Chromates, **carbonates**, and **phosphates** are insoluble in this group. There are no carbonates of mercury, arsenic, antimony, or tin and no chromates or phosphates of arsenic or antimony. Stannous ions and antimonous compounds can reduce chromates in acid solution, and precipitates of normal chromates are formed with silver, mercury, and lead only.

The Second Main Group

The second natural group of cations in the sulphide scheme of analysis consists of those cations whose sulphides are either precipitated by hydrogen sulphide in neutral or alkaline solution, or are hydrolysed to insoluble hydroxides under these conditions. On referring to **Tables II** and **IIIA** (pp. 219 and 221) it is not surprising to find that whereas the sulphides of stannous tin, lead, and cadmium are the most soluble of those in the first main group, the sulphides of zinc and its much rarer neighbours in the periodic table are the least soluble of the second main group, and can in fact be precipitated in solutions containing *weak* acids (e.g. acetic acid) but not in solutions containing any appreciable quantity of hydrogen ion.

Further, it is of interest to note that nickel and cobalt form polymorphic sulphides; in each case there is a form soluble in dilute hydrochloric acid and at least one more stable form insoluble in it. Elements in the first long period to the right of the line dividing chromium from manganese form sulphides stable in the presence of water; elements to the left of it form sulphides which are hydrolysed by water. The hydroxides and 'hydrosulphides' of the alkali and alkaline earth metals are sufficiently soluble not to be precipitated in this analytical group.

The cations usually included in elementary work in this group are the ZINC, NICKEL, COBALT, FERROUS, FERRIC, MANGANOUS, CHROMIC, and ALUMINIUM ions. The chlorides and iodides of these cations are all soluble in or hydrolysed by water and are therefore not used in precipitation tests. (Ferric iodide is not known.) The sulphates are also soluble; the chromates do not give particularly distinctive reactions. On the other hand the behaviour of the *hydroxides*, *sulphides*, and *phosphates* is particularly important in this group. Carbonates of the trivalent ions ($Al^{\cdots}$, $Fe^{\cdots}$, $Cr^{\cdots}$) do not exist; a basic but not the normal aluminium chromate is known, and there is no chromic chromate.

Zinc

Zinc forms a single oxide ZnO which is white when cold but turns yellow on heating. It is very stable to heat. The zinc ion is divalent, colourless, and stable, the solubilities of its salts such as are generally expected for salts of a 'heavy metal'.

PRINCIPAL REACTIONS (*use a solution of zinc nitrate or sulphate*).

1. Sodium hydroxide solution added to a solution of a zinc salt gives a white gelatinous precipitate of zinc hydroxide, soluble in excess alkali with formation of sodium zincate:

$$Zn(OH)_2+2NaOH = Na_2ZnO_2+2H_2O.$$

As zinc shows no higher valency than two in its compounds, the hydroxide is unchanged by oxidizing agents in solution.

2. Ammonium hydroxide solution also precipitates zinc hydroxide which is soluble in excess of the precipitant, in this case because of the formation of a complex cation with a soluble hydroxide:

$$Zn^{\cdot\cdot}+6NH_3 = [Zn(NH_3)_6]^{\cdot\cdot}.$$

The addition of ammonium chloride solution (or other ammonium salts) to the ammonium hydroxide used for precipitation represses its dissociation and reduces in consequence the concentration of hydroxyl ion (see p. 19). The *solubility product* of zinc hydroxide is consequently not reached. If therefore ammonium chloride solution followed by ammonium hydroxide solution be added to a solution of a zinc salt no precipitate of zinc hydroxide will be formed. Alternatively, in the absence of caustic alkali, zinc hydroxide will dissolve in ammonium chloride solution. Naturally this will not occur in the presence of a fully dissociated source of hydroxyl ion such as sodium hydroxide. The formation of 'double salts' (i.e. with unstable complex ions) in concentrated solutions of ammonium chloride may also affect the solubility of otherwise insoluble substances, particularly hydroxides. This was the explanation of abnormal solubilities given before the ionic dissociation theory was fully developed and is probably partly true.

3. Hydrogen sulphide added to a neutral or alkaline solution of a zinc salt gives a white precipitate of zinc sulphide ZnS.

It does not matter whether the solution is that of an alkaline zincate or whether it is made alkaline by ammonium hydroxide in the presence of ammonium chloride. The alkalinity of the solution is in favour of a high concentration of sulphide ions and there is sufficient zinc ion present in each case for the solubility product of zinc sulphide to be exceeded.

4. Zinc sulphate is soluble. Ammonium carbonate precipitates a basic carbonate soluble in excess of the precipitant or in solutions of ammonium salts.

5. Sodium hydrogen phosphate solution gives a white precipitate of zinc phosphate which is soluble in dilute acids. This precipitate is soluble in ammonium hydroxide solution or in sodium hydroxide solution, which removes zinc ion as ZnO_2'' so that the solubility product of the zinc phosphate is no longer exceeded.

In the presence of ammonium salts sodium hydrogen phosphate solution precipitates *zinc ammonium phosphate* $ZnNH_4PO_4$ which is used for the quantitative determination of zinc, as on ignition it is converted into stable *zinc pyrophosphate* $Zn_2P_2O_7$.

Special Reaction

6. Potassium ferrocyanide solution gives a white precipitate of zinc ferrocyanide.

Dry Tests

When heated with alkali carbonate on charcoal zinc compounds give an incrustation of zinc oxide which is yellow when hot but white when cold. If the oxide residue be touched with a drop of cobalt nitrate solution and again heated a *green* mass is formed (*Rinmann's Green*).

Nickel

The normal oxide for salts is the stable green NiO. The black nickelic oxide Ni_2O_3 does not form salts. There is also an unstable Ni_3O_4. The hydrated ion is green, its valency is two and there is nothing exceptional in the solubilities of its commoner salts. The insolubility of the sulphide and more particularly of the cyanide and complex cyanides is made use of in anion identification. The anhydrous salts are usually yellow.

Principal Reactions (*use a solution of nickel nitrate*).

1. Sodium hydroxide solution gives with a solution of a nickel salt a green precipitate of nickel hydroxide $Ni(OH)_2$, insoluble in excess of sodium hydroxide solution (*not* amphoteric). The hydroxide can be oxidized to the higher oxide by sodium hypochlorite solution but is unaffected by hydrogen peroxide. The higher oxide Ni_2O_3 is dark brown when hydrated.

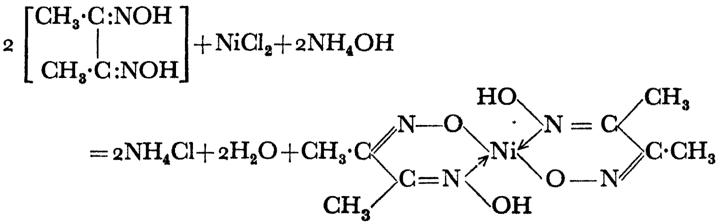
2. Ammonium hydroxide solution precipitates a green basic salt, soluble in excess of the precipitant owing to the formation of a complex blue cation $(Ni(NH_3)_6]^{\cdot\cdot}$ with a soluble hydroxide. Ammonium chloride solution prevents the precipitation of nickel hydroxide by ammonium hydroxide (cf. **Zinc 2**).

3. Hydrogen sulphide added to a neutral or alkaline solution of a nickel salt gives a black precipitate of nickel sulphide NiS. The initial precipitate is soluble in dilute hydrochloric acid, but on being left for a few minutes in a cold solution of hydrogen sulphide it is converted into a form much less soluble in acid.

4. Nickel sulphate is soluble; the carbonate and phosphate are insoluble in water but readily soluble in acid. Nickel carbonate is soluble in excess of ammonium carbonate.

SPECIAL REACTIONS

5. Dimethylglyoxime forms a bright red nickel derivative which is very insoluble in faintly alkaline solution. It is precipitated when an alcoholic solution of dimethylglyoxime is added to a solution of a nickel salt which is then made just alkaline with ammonium hydroxide. The importance of this test lies in the fact that dilute solutions containing cobalt give no precipitate under these conditions.



$$2\begin{bmatrix} CH_3{\cdot}C{:}NOH \\ | \\ CH_3{\cdot}C{:}NOH \end{bmatrix} + NiCl_2 + 2NH_4OH$$

6. Potassium cyanide solution gives a pale green precipitate of nickel cyanide which dissolves in excess of the cyanide solution with formation of a complex anion $[Ni(CN)_4]''$. This solution contains sufficient nickel ions for their oxidation by hypochlorite to be fairly rapid.

DRY TESTS

When heated with alkali carbonate on charcoal nickel salts give finely divided nickel, which is slightly magnetic, with no oxide incrustation.

Borax bead: oxidizing flame *brown*; reducing flame *grey*.

Cobalt

The normal oxide for salts is CoO (grey-green); there is an intermediate oxide Co_3O_4 (black), and also a cobaltic oxide Co_2O_3 (dark brown or black) of which only complex derivatives are stable. The salt-forming cobalt ion is divalent and the hydrated ion is pink though it shows remarkable colour changes when forming complex ions in solution. The resulting ions are usually blue or some shade of purple.

PRINCIPAL REACTIONS (*use a solution of cobalt nitrate*).

1. Sodium hydroxide solution precipitates a blue basic salt from a solution of a cobalt salt:

$$Co(NO_3)_2 + NaOH = Co(OH)NO_3 + NaNO_3.$$

On adding excess alkali, or on warming the precipitate, the basic salt is converted completely into pink cobaltous hydroxide; vigorous heating of the precipitate in contact with air converts it to the brown cobaltic hydroxide $Co(OH)_3$. Hydrogen peroxide or any other strong oxidizing agent rapidly effects this change in alkaline solution.

2. Ammonium hydroxide solution precipitates a basic salt which is soluble in excess of ammonium hydroxide solution (cf. **Nickel 2**) and in ammonium chloride solution (cf. **Zinc 2**).

The brown complex ion formed by the co-ordination of ammonia on to a cobaltous ion is oxidized slowly in contact with air to the more stable *cobaltic* complex, containing trivalent cobalt.

3. Hydrogen sulphide added to a neutral or alkaline solution of a cobalt salt precipitates black cobalt sulphide CoS.

Like nickel sulphide, this precipitate is eventually converted into a form insoluble in dilute hydrochloric acid.

4. Cobalt sulphate is soluble in water. Ammonium carbonate precipitates a red basic salt soluble in excess of the precipitant. Sodium phosphate solution in the presence of ammonium salts precipitates a cobalt ammonium phosphate which can be used for quantitative determination of cobalt. Cobaltous phosphate is soluble in acids but is reprecipitated on the addition of ammonium hydroxide.

Special Reactions

5. Potassium nitrite precipitates from solutions of cobalt salts acidified with acetic acid yellow potassium cobaltinitrite. Nitric oxide is evolved.

$$Co^{\cdot\cdot}+7NO_2'+3K^{\cdot}+2H^{\cdot} = K_3[Co(NO_2)_6]+NO+H_2O.$$

6. With solutions containing cobalt ions, α-nitroso-β-naphthol, dissolved in acetic acid (50 per cent.), gives a purple-brown precipitate of its cobalt derivative insoluble in dilute acids. No such precipitate is given with dilute solutions of nickel salts.

7. A concentrated solution of ammonium thiocyanate gives a blue coloration with cobalt salts owing to the formation of a complex anion $[Co(CNS)_4]''$. The blue colour disappears on dilution owing to dissociation of the complex ion. The undissociated blue compound can be extracted from the solution by amyl alcohol.

8. Potassium cyanide solution gives a red-brown precipitate of cobaltous cyanide which dissolves in excess of potassium cyanide solution to form potassium cobaltocyanide. This is readily oxidized on boiling the solution and the complex ion formed containing trivalent cobalt (cobalticyanide ion $[Co(CN)_6]'''$) is stable enough to resist oxidation by hypochlorite except on prolonged boiling.

Dry Tests

When heated with alkali carbonate on charcoal cobalt compounds give the finely divided metal, which is feebly magnetic, with no visible oxide.

Borax bead: blue in both oxidizing and reducing flames.

Iron

Iron forms (*a*) ferrous oxide FeO (black), obtained pure only with great difficulty, easily oxidized and easily reduced; it corresponds to the **ferrous** salts; (*b*) ferric oxide Fe_2O_3 (red), extremely stable but turning black on heating; it corresponds to the **ferric** salts: (*c*) an intermediate oxide Fe_3O_4 ('lodestone' or *magnetic oxide* also black) which is converted by acids to mixtures of ferrous and ferric salts. Iron is divalent in the ferrous compounds and trivalent in the ferric compounds. The hydrated ferrous ion is green; the hydrated ferric ion is yellow. The anhydrous compounds vary considerably in colour. The solubilities of the characteristic compounds of both ions are quite normal. Ferrous and ferric ions are both fairly stable in solution, but ferrous oxide and hydroxide are very readily oxidized, while ferric carbonate is too unstable to exist. The existence of ferric sulphide is disputed. Moist ferrous carbonate is readily oxidized with decomposition to hydrated ferric oxide. Hydrolysis occurs with salts of both ions, and insoluble basic salts can often be prepared by boiling solutions containing ferric ions. The use of ferrous and ferric ions in the identification of anions should be noted.

PRINCIPAL REACTIONS OF THE FERROUS ION (*use a solution of ferrous sulphate in dilute sulphuric acid*).

1. *In complete absence of air* (i.e. from boiled solutions) sodium hydroxide solution precipitates white ferrous hydroxide $Fe(OH)_2$ which is insoluble in excess alkali. It is readily oxidized by the air to hydrated ferric oxide, and usually appears as a dirty green precipitate when ordinary solutions are used for its precipitation. The addition of hydrogen peroxide rapidly completes the conversion to ferric hydroxide.

Ammonium hydroxide gives the same precipitate, but not in the presence of a large concentration of ammonium ions. In the presence of air, however, the oxidized precipitate forms, as this is insoluble even when the ammonium-ion concentration is high.

2. Hydrogen sulphide added to a neutral or alkaline solution of a ferrous salt gives a black precipitate of ferrous sulphide FeS, readily soluble in dilute hydrochloric acid. Precipitation is not complete unless the solution is definitely alkaline.

3. Ammonium carbonate solution gives a white precipitate of ferrous carbonate which is readily oxidized in the presence of air to the brown hydrated ferric oxide:

$$4FeCO_3+6H_2O+O_2 = 4CO_2+4Fe(OH)_3.$$

Ferrous bicarbonate can probably exist in solution.

4. Sodium phosphate solution gives a precipitate of ferrous phosphate which is soluble in dilute acids . (It must be oxidized for the purposes of the phosphate separation in analysis of mixtures.)

SPECIAL REACTIONS

5. Potassium ferrocyanide solution gives a white precipitate of potassium ferrous ferrocyanide $K_2Fe[Fe(CN)_6]$ invariably contaminated with its blue oxidation product. The resulting colour is a pale blue.

6. Potassium ferricyanide gives a dark blue precipitate, known as Turnbull's blue, which is principally ferrous ferricyanide.

PRINCIPAL REACTIONS OF THE FERRIC ION (*use a solution of ferric chloride*).

1. Sodium hydroxide solution added to a solution of a ferric salt precipitates red-brown ferric hydroxide $Fe(OH)_3$, insoluble in excess of the precipitant. Ammonium hydroxide has the same action. The hydroxide is precipitated by a very small concentration of hydroxyl ions and is therefore not dissolved by solutions of ammonium salts (cf. **Zinc 2**). The precipitate is unaffected by the addition of hydrogen peroxide solution.

2. When hydrogen sulphide is added to an acid solution containing ferric ions, these are reduced to ferrous ions, and sulphur is deposited:

$$2\text{Fe}^{\cdots}+\text{H}_2\text{S} = 2\text{Fe}^{\cdot\cdot}+2\text{H}^{\cdot}+\text{S}.$$

If a solution containing ferric ions is made alkaline, ferric hydroxide will be precipitated, and if hydrogen sulphide be added to this, the brown hydroxide will change to the even less soluble black ferric sulphide (which may possibly be decomposed to ferrous sulphide and sulphur).

3. Ammonium carbonate solution gives a brown precipitate of a basic character which readily decomposes on warming to give ferric hydroxide.

4. Sodium hydrogen phosphate solution gives a pale yellow precipitate of ferric phosphate FePO_4, soluble in dilute hydrochloric acid but insoluble in acetic acid. Complete precipitation of either ferric ion or phosphate ion as ferric phosphate is only accomplished in the presence of a large concentration of acetate ions or similar *weak acid* anions which lower the hydrogen-ion concentration. The precipitate is appreciably soluble in ferric acetate solution.

Special Reactions.

5. Sodium acetate solution gives a reddish-brown coloration with solutions of ferric salts. On boiling the solution the iron is precipitated as basic ferric acetate.

$$\text{Fe}(\text{CH}_3\text{COO})_3+2\text{H}_2\text{O} = 2\text{CH}_3\text{COOH}+\text{Fe}(\text{OH})_2(\text{CH}_3\text{COO}).$$

Reactions **4** and **5** are combined for the removal of the phosphate radical from solutions in which it interferes with the normal course of analysis.

6. Potassium ferrocyanide solution gives a deep blue precipitate of ferric ferrocyanide (Prussian blue).

Potassium ferricyanide merely intensifies the brown colour of the solution containing ferric ions owing to an increase in their concentration:

$$K_3[Fe(CN)_6]+FeCl_3 \rightleftharpoons 3KCl+2Fe(CN)_3.$$

7. Potassium thiocyanate solution gives a blood-red coloration of ferric thiocyanate which is only very slightly ionized, and on account of this is soluble in ether.

DRY TESTS

When heated with alkali carbonate on charcoal, iron compounds leave the metal in a finely divided state with no incrustation of oxide.

Borax bead: yellow when hot in the oxidizing flame; green in the reducing flame.

Manganese

The normal oxide for manganous salts is the readily oxidized greenish-black MnO. The brown oxide Mn_2O_3 corresponding to the manganic salts and the red-brown intermediate oxide Mn_3O_4, which gives rise to manganous salts and manganese dioxide on treatment with acid, are more stable. Manganese dioxide MnO_2 (pyrolusite) is the most important oxide; it gives oxygen with difficulty on heating, but liberates chlorine readily from hydrochloric acid with formation of manganous chloride $MnCl_2$. Two very unstable acidic oxides, MnO_3 and Mn_2O_7, can be made and correspond to the manganates (green) and the permanganates (purple), q.v.

The only stable simple cation formed by manganese is the divalent manganous ion. The trivalent manganic ion, corresponding to the ferric ion, is not nearly so stable as the latter, and does not exist under ordinary analytical conditions. The anions formed by manganese are discussed on p. 74. The hydrated manganous ion has a very pale pink colour. The solubilities of its salts show no striking abnormalities.

PRINCIPAL REACTIONS (*use a solution of manganous chloride*).

1. Sodium hydroxide solution, when added to a solution of a manganous salt, gives a white precipitate of manganous hydroxide $Mn(OH)_2$, insoluble in excess of the precipitant, and readily oxidized by the air or any oxidizing agent to hydrated manganese dioxide (brown) or intermediate stages of oxidation. Hydrogen peroxide effects this oxidation rapidly.

The precipitate of manganous hydroxide formed by adding ammonium hydroxide to a solution of a manganous salt is redissolved by the addition of a large concentration of ammonium ions, e.g. in ammonium chloride solution (cf. **Zinc 2**).

2. The addition of hydrogen sulphide to an alkaline solution containing manganous ions gives a pale pinkish-yellow precipitate of hydrated manganese sulphide. The pure anhydrous form is green.

3. Ammonium carbonate solution gives a white precipitate of manganous carbonate, insoluble in excess of the reagent or in the presence of ammonium salts.

4. Sodium hydrogen phosphate solution gives a white precipitate of normal manganese phosphate, and in the presence of ammonium compounds, the double manganese ammonium phosphate is precipitated, which on ignition gives manganese pyrophosphate. This can be used for the gravimetric determination of manganese.

$$2MnNH_4PO_4 = Mn_2P_2O_7 + H_2O + 2NH_3.$$

SPECIAL REACTIONS

5. Many sensitive tests for manganese depend upon the oxidation of the manganous ion to the intensely coloured permanganate ion MnO_4'. The simplest of these is to add a *little* of the solid or solution to be tested to a small quantity of red lead and then boil with a little moderately concentrated nitric acid (lead dioxide should do as well as red lead, but the commercial product sometimes fails to give good results). The residue of unattacked lead dioxide is allowed to settle, and the supernatant liquid, diluted if necessary, will show the characteristic permanganate colour.

$$2Mn^{\cdot\cdot}+5PbO_2+4H^{\cdot} = 5Pb^{\cdot\cdot}+2H_2O+2MnO_4'.$$

It must be observed that the manganous ion can reduce the permanganate ion under certain conditions with formation of manganese dioxide or of manganites of certain cations. A large excess of manganous ion in this test may therefore tend to prevent the permanganate formation.

6. Manganous compounds on fusion with alkali (sodium hydroxide) in the presence of an oxidizing agent (e.g. potassium chlorate) give a green melt containing alkali manganate.

DRY TEST

Borax bead: amethyst.

Chromium

The normal oxide for chromic salts is the green Cr_2O_3. Chromous oxide (black) is even more readily oxidized than ferrous or manganous oxides. The acid oxide CrO_3 which forms deliquescent red crystals gives rise to the chromates and dichromates which are discussed on p. 72. Chromium in chromic salts is trivalent; the hydrated ion is green, but it forms many complex ions, both with anions and with molecules of solvent, which vary in colour but are usually green or violet. The blue divalent *chromous* ion is such an efficient reducing agent that it is readily converted to the chromic ion in solution at the expense of the hydrogen ion of the water, i.e. it tends to liberate hydrogen as a metal does. It is not therefore encountered in the usual course of analysis. The solubilities of the characteristic chromic compounds are normal, but the *anhydrous* chloride $CrCl_3$ can be obtained in a quite insoluble form of a unique violet-pink colour. This will dissolve in water only in the presence of a small quantity of chromous ion.

PRINCIPAL REACTIONS (*use a solution of chromic chloride*).

1. The addition of sodium hydroxide solution to a solution containing chromic ions gives a grey-green precipitate of chromic hydroxide soluble in excess of the precipitant in the cold. The green solution formed contains *sodium chromite.*

$$Cr(OH)_3 + NaOH \rightleftharpoons NaCrO_2 + 2H_2O.$$

This rather unstable compound is hydrolysed in solution and on boiling the hydrolysis is increased. A precipitate which may be regarded as a basic chromite forms. It is sometimes described as an insoluble form of the hydroxide, but it always contains alkali.

The addition of hydrogen peroxide to the solution of sodium chromite, or to a suspension of the basic precipitate, results in the formation of a yellow solution of sodium chromate, which may be further identified by the perchromate reaction (**Chromates 4**).

$$2CrO_2' + 3H_2O_2 + 2OH' = 2CrO_4'' + 4H_2O.$$

2. Ammonium hydroxide solution gives with chromic salts a precipitate of chromic hydroxide, which is insoluble in excess ammonium hydroxide solution or in solutions of ammonium salts, i.e. the hydroxide has a very low solubility product (cf. the other trivalent hydroxides in this group, $Al(OH)_3$, $Fe(OH)_3$).

3. The addition of hydrogen sulphide to a suspension of chromic hydroxide has no effect, as chromic sulphide is completely hydrolysed by water, and therefore will not form in these circumstances.

4. Sodium hydrogen phosphate solution gives a green precipitate of normal chromic phosphate, $CrPO_4$, soluble in dilute mineral acids, and in dilute acetic acid.

SPECIAL REACTION

5. Chromic ions in acid solution are reduced slowly by zinc to blue chromous ions. If the solution containing chromous ions is filtered into a concentrated solution of sodium acetate, a characteristic reddish-purple precipitate of chromous acetate will form.

DRY TEST

Borax bead: green in both oxidizing and reducing flames.

Aluminium

The only oxide of aluminium is the white infusible oxide Al_2O_3, which is extremely stable. The ion is trivalent and colourless. It reacts with water and its normal salts in solution give evidence of this hydrolysis by their acid reaction. In many cases hydrolysis proceeds so far that the insoluble hydroxide separates. The only compounds of this ion therefore which can exist in the presence of water are those which are soluble salts of strong acids (chloride, nitrate, sulphate, &c.) and those which are less soluble than the hydroxide.

PRINCIPAL REACTIONS (*use a solution of aluminium nitrate*).

1. Sodium hydroxide solution added to a solution containing aluminium ions produces a white gelatinous precipitate of aluminium hydroxide readily soluble in excess of the precipitant. The solution contains sodium aluminate $NaAlO_2$. Unlike the corresponding solution of chromic hydroxide this solution is not affected by boiling. From the ionic equation

$$OH' + Al(OH)_3 \rightleftharpoons AlO_2' + 2H_2O$$

it is obvious that a lowering of the concentration of hydroxyl ions will reprecipitate the hydroxide. The addition of ammonium chloride is sufficiently effective for this purpose, and aluminium hydroxide can be completely precipitated from a solution of sodium aluminate by boiling the latter with a solution of ammonium chloride.

$$\begin{aligned} &AlO_2' + NH_4^{\cdot} + H_2O \\ &\qquad = Al(OH)_3 + NH_3 \text{ (\textit{removed by boiling})}. \end{aligned}$$

As aluminium is invariably trivalent, the hydroxide is not affected by oxidizing agents such as hydrogen peroxide.

2. Ammonium hydroxide solution gives a precipitate of aluminium hydroxide, but cannot redissolve it; nor is the hydroxide soluble enough to stay in solution in the presence of a large concentration of ammonium ions (e.g. in ammonium chloride solution). Aluminium hydroxide forms a colloidal solution in water but this gradually coagulates in the presence of electrolytes, especially on heating.

As aluminium sulphide is completely hydrolysed by water (i.e. the hydroxide is less soluble than the sulphide), the addition of hydrogen sulphide to a suspension of aluminium hydroxide has no effect.

3. Sodium hydrogen phosphate solution gives a colourless precipitate of normal aluminium phosphate $AlPO_4$, soluble in dilute mineral acids but insoluble in acetic acid (cf. ferric phosphate and chromic phosphate).

Aluminium phosphate is readily soluble in sodium hydroxide solution as the $Al^{\cdot\cdot\cdot}$ ions are removed as AlO_2' ions and the solubility product $[Al^{\cdot\cdot\cdot}]$ $[PO_4''']$ is no longer exceeded (cf. $Zn_3(PO_4)_2$). Boiling the solution with ammonium chloride solution will naturally reprecipitate the phosphate, but the precipitate will contain some aluminium hydroxide.

DRY TESTS

When heated with alkali carbonate on charcoal aluminium salts form a white mass, which is incandescent when hot and forms a blue compound (Thénard's blue) when heated with a drop of cobalt nitrate solution.

The Second Main Group: Summary

1. The **chlorides** and **iodides** of this group are all soluble. Aluminium and ferric chlorides and aluminium iodide are considerably hydrolysed, and their solutions show a definitely acid reaction in consequence. Ferric and chromic iodides do not exist.

2. The **hydroxides** of all these cations are insoluble in water. If the solubility product of a hydroxide $[X^{\cdot}][OH']$ or $[X^{\cdot\cdot}]\,[OH']^2$ or $[X^{\cdot\cdot\cdot}]\,[OH']^3$ is less than 10^{-7}, 10^{-14}, or 10^{-21} respectively, then the minimum concentration of hydroxyl ion necessary for precipitation from a normal solution of the cations will be less than 10^{-7}, i.e. precipitation will begin while the solution is still acid. This applies to aluminium hydroxide, ferric hydroxide (S.P. $= 1{\cdot}1 \times 10^{-36}$), and chromic hydroxide. With zinc hydroxide (S.P. $= 1{\cdot}8 \times 10^{-14}$), manganese hydroxide (S.P. $= 4 \times 10^{-14}$), nickel, cobalt, and ferrous hydroxide (S.P. $= 1{\cdot}6 \times 10^{-14}$) it is possible to get a concentration of hydroxyl ion which is on the alkaline side of neutrality (10^{-7}) and yet not sufficient for precipitation. For instance, the minimum hydroxyl ion concentration for precipitation of zinc hydroxide is about $1{\cdot}4 \times 10^{-7}$ if the zinc ion concentration is normal, or $1{\cdot}4 \times 10^{-6}$ for $0{\cdot}01\ N$ zinc ion. Such concentrations are obtained by adding an excess of ammonium ions to ammonium hydroxide solution to repress its ionic dissociation, and the more soluble hydroxides are therefore quite soluble in ammonium chloride solution.

Of the group hydroxides, those of aluminium, chromium, and zinc are soluble in an excess of sodium hydroxide solution, but a basic chromite is precipitated on boiling the solution containing chromium. Zinc and nickel hydroxides are soluble and chromic hydroxide somewhat soluble in ammonium hydroxide solution owing to complex cation formation.

Hydrogen peroxide has no effect on zinc, aluminium, nickel, or ferric hydroxides, but causes oxidation of 'ferrous hydroxide' (dirty green) to ferric hydroxide (brown), of chromic hydroxide (green) in the presence of alkali to alkali chromate solution (yellow), of manganous hydroxide (white) to hydrated manganese dioxide (dark brown), and of cobalt hydroxide (pink) to cobaltic oxide (black).

3. The **sulphides** of zinc, nickel, cobalt, iron, and manganese are insoluble in water but soluble in 0·25 *N* acid. Nickel and cobalt sulphides have polymorphic forms which are insoluble in 0·25 *N* acid. Aluminium and chromium sulphides are hydrolysed by water with formation of hydroxides insoluble in water or in solutions of ammonium salts.

4. The **sulphates** of these cations are soluble in water. The **chromates** are rather peculiar in their behaviour. Basic precipitates are readily obtained with ferric and aluminium ions and under certain conditions with cobalt and zinc. Normal ferrous and manganous chromates do not appear to exist owing to interaction of the anion and cation, and there is no normal aluminium chromate. Doubtful intermediate oxides of chromium are sometimes referred to as chromic chromates. The normal chromates of zinc, nickel, and cobalt are insoluble when prepared away from water, but are not precipitated by potassium chromate.

6. Carbonates. These exist only with the divalent cations of this group, and are all insoluble in water. Basic carbonates are usually precipitated by sodium carbonate solution.

7. The normal **phosphates** of this group are all insoluble in water, but soluble in dilute mineral acid, and, with the exception of aluminium and ferric phosphates, soluble in acetic acid. In addition the phosphates of aluminium, chromium, and zinc are soluble in excess of sodium hydroxide solution, while zinc and nickel phosphates are soluble in excess of ammonium hydroxide solution (cf. hydroxides). In the presence of ammonium salts the very insoluble zinc ammonium phosphate $ZnNH_4PO_4$ and manganese ammonium phosphate $MnNH_4PO_4$ can be precipitated.

The behaviour of phosphates in this group is important since all the normal salts are insoluble in water but soluble in dilute mineral acid. In the alkaline solution necessary for group precipitation, the phosphates of the group cations may be precipitated along with the phosphates of barium, strontium, calcium, and magnesium, should these ions be present. The presence of phosphate ion need not interfere with the identification of cations in the Second Main Group since the typical group precipitates are more insoluble, under the conditions of analysis, than the phosphates; any treatment which will dissolve a typical group precipitate by lowering the concentration of cations will naturally redissolve the corresponding phosphate also (e.g. the treatment of $Al(OH)_3$ or $Zn(OH)_2$ with excess sodium hydroxide). In case barium, strontium, calcium, or magnesium are present, however, the phosphate ion must be removed. A simple method for doing this depends upon the insolubility of ferric phosphate in acetic acid. The presence or absence of iron is established independently of the group analysis by the use of potassium ferrocyanide, and the phosphate ion precipitated by the addition of ferric chloride in the presence of ammonium acetate and acetic acid. If the solution is now boiled the residual iron is precipitated as basic ferric acetate. (See **Ferric ion 4** and **5**.) This precipitate of ferric phosphate and basic acetate will also contain most of the aluminium present and some of the chromium, for although chromic phosphate is soluble in cold acetic acid (i.e. more soluble than ferric phosphate), it is reprecipitated on boiling, and although it is not precipitated when alone as basic acetate it is carried down when the basic acetates of iron and aluminium are precipitated. With excess of chromium present some of the iron and aluminium may remain in the filtrate.

The Third Main Group

The remaining cations are those whose sulphides are hydrolysed in dilute alkaline solution to give soluble hydroxides or 'hydrosulphides'. They include the elements in Groups I A and II A of the periodic table (see **Table III**, p. 220). Those considered here are BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, POTASSIUM, and SODIUM. The chlorides and iodides of this group are also soluble, so that analytical procedure is concerned mainly with the behaviour of the sulphates, chromates, carbonates, and phosphates. Note that these are the precipitates which are relatively unimportant in the other two main groups. The ions of this group are all colourless. Those of Group I A are monovalent; those of Group II A are divalent. The use of barium and calcium salts in anion identification should be noted.

Barium

Barium forms a normal oxide BaO 'baryta' which is white, and a white peroxide BaO_2 which is a true peroxide, i.e. gives hydrogen peroxide on treatment with dilute acid. The peroxide gives off oxygen on heating.

PRINCIPAL REACTIONS (*use a solution of barium chloride or nitrate*).

1. Sodium hydroxide solution will precipitate white barium hydroxide $Ba(OH)_2$ from a solution containing a high concentration of barium ions. The solubility of barium hydroxide at 20° is 3·89 gm. in 100 of water or 0·23 gram equivalents per litre. Ammonium hydroxide solution never contains sufficient hydroxyl ions to precipitate such a relatively soluble hydroxide.

2. Dilute sulphuric acid gives a dense white precipitate of barium sulphate $BaSO_4$ practically insoluble in all acids except concentrated sulphuric acid. It is also insoluble in ammonium sulphate solution.

Calcium sulphate solution contains sufficient sulphate ions to give a similar precipitate immediately on addition (cf. **Strontium 2**).

3. Potassium chromate solution gives a pale yellow precipitate of barium chromate $BaCrO_4$ which is soluble in dilute mineral acids but insoluble in acetic acid.

4. Ammonium carbonate solution gives a white precipitate of barium carbonate $BaCO_3$, readily soluble with decomposition in acids.

The precipitate is somewhat soluble in water containing (as it usually does) free carbonic acid, owing to the formation of a soluble bicarbonate:

$$BaCO_3 + H_2CO_3 = Ba(HCO_3)_2.$$

Precipitation is therefore best completed by boiling the solution, but it should be remembered that boiling in the presence of ammonium salts will tend to redissolve the barium carbonate owing to the reversibility of the equations:

$$BaCO_3 \rightleftharpoons Ba^{\cdot\cdot} + CO_3''$$

$$CO_3'' + 2NH_4^{\cdot} \rightleftharpoons 2NH_3 + H_2O + CO_2.$$

5. Sodium hydrogen phosphate solution gives a white precipitate of barium hydrogen phosphate $BaHPO_4$, which is converted by ammonium hydroxide to the normal salt $Ba_3(PO_4)_2$. Both precipitates are soluble in dilute mineral acids.

SPECIAL REACTIONS

6. Ammonium oxalate solution gives a white precipitate of barium oxalate, very slightly soluble in water, and soluble in hot dilute acetic acid as well as in mineral acids.

7. Concentrated hydrochloric acid will precipitate barium chloride from solutions containing moderately high concentrations of this salt ('common ion effect'). When barium chloride is used for identifying a sulphate, a precipitate formed in the presence of *concentrated* hydrochloric acid is not conclusive.

DRY TESTS

When heated with alkali carbonate on charcoal, barium salts leave the white incandescent oxide or the carbonate.

Flame: apple green tinged with yellow.

Strontium

The normal oxide SrO (white) and the peroxide SrO_2 (white) are similar to those of barium.

PRINCIPAL REACTIONS (*use a solution of strontium nitrate*).

1. The hydroxide $Sr(OH)_2$ is rather less soluble than that of barium and is precipitated under similar conditions.

2. Dilute sulphuric acid gives a white precipitate of strontium sulphate $SrSO_4$, insoluble in dilute acids and in ammonium sulphate solution. Calcium sulphate solution causes a slow precipitation of strontium sulphate from dilute solutions of a strontium salt.

3. Potassium chromate will precipitate strontium chromate $SrCrO_4$ from *concentrated solutions only*. The precipitate is soluble in acetic acid.

4. Ammonium carbonate solution gives a white precipitate of strontium carbonate $SrCO_3$ soluble with decomposition in dilute acids. It is also soluble to some extent in carbonic acid and in boiling solutions of ammonium salts (cf. **Barium 4**).

5. Sodium hydrogen phosphate precipitates white strontium hydrogen phosphate, soluble in dilute mineral acids.

SPECIAL REACTION

6. Ammonium oxalate solution gives a white precipitate of strontium oxalate soluble in dilute mineral acids, but only slightly soluble in acetic acid.

DRY TESTS

When heated with alkali carbonate on charcoal, strontium salts leave a white incandescent residue of oxide.

Flame: bright red.

Calcium

The normal oxide for salts is quicklime CaO (white): there is also a white peroxide CaO_2 similar to barium peroxide.

Principal Reactions (*use a solution of calcium chloride*).

1. Calcium hydroxide is less soluble than strontium or barium hydroxides, but is precipitated under similar conditions. It is more soluble in cold water than in hot, the solubility at 10° being 0·29 gm. and at 100° 0·06 gm. in 100 gm. of water.

2. Dilute sulphuric acid will not precipitate calcium sulphate from a solution containing a moderate concentration of calcium ions, but the addition of alcohol will effect the precipitation. Concentrated sulphuric acid will precipitate, and, in excess, will redissolve calcium sulphate $CaSO_4$, owing to the formation of a soluble acid salt. The precipitate is also soluble in concentrated ammonium sulphate solution, owing to the formation of a complex anion which lowers the concentration of the calcium ions.

$$Ca^{\cdot\cdot}+2SO_4''+2NH_4^{\cdot} = 2NH_4^{\cdot}+[Ca(SO_4)_2]''.$$

3. Potassium chromate solution precipitates calcium chromate from very concentrated solutions only, and not at all in the presence of an acid.

4. Ammonium carbonate solution gives a white precipitate of calcium carbonate $CaCO_3$ soluble with decomposition in practically all acids. It is also dissolved by free carbonic acid to form soluble calcium bicarbonate $Ca(HCO_3)_2$ and is appreciably soluble in boiling solutions of ammonium salts (cf. **Barium 4**).

5. Sodium hydrogen phosphate solution precipitates white, insoluble, calcium hydrogen phosphate $CaHPO_4$ which is converted by ammonium hydroxide to the normal phosphate $Ca_3(PO_4)_2$.

SPECIAL REACTION

6. Ammonium oxalate solution precipitates white calcium oxalate soluble in mineral acids but practically insoluble in acetic acid.

DRY TESTS

When heated with alkali carbonate on charcoal the salts of calcium leave a white incandescent oxide (cf. 'lime-light').

Flame: brick-red.

Magnesium

The only oxide of magnesium is the normal oxide MgO (white).

PRINCIPAL REACTIONS (*use a solution of magnesium nitrate*).

1. Sodium hydroxide solution gives a white gelatinous precipitate of magnesium hydroxide $Mg(OH)_2$ which is soluble in solutions of ammonium salts provided there is not excess of a strong base present.

2. Magnesium sulphate and magnesium chromate are both easily soluble in water.

3. Ammonium carbonate solution gives a white precipitate of basic magnesium carbonate which is readily soluble in acids and in a solution of ammonium chloride. It is also dissolved by free carbonic acid to form magnesium bicarbonate (cf. **Barium 4**).

4. Sodium hydrogen phosphate solution gives a white precipitate of normal magnesium phosphate, but in the presence of ammonium ions magnesium ammonium phosphate $MgNH_4PO_4$ is usually precipitated. On ignition this leaves the stable pyrophosphate $Mg_2P_2O_7$ (cf. **Zinc 5**).

SPECIAL REACTIONS

5. If to an acidic solution containing magnesium ions are added a few drops of *p*-nitrobenzene-azo-resorcinol in sodium hydroxide solution, and the whole made alkaline with more sodium hydroxide, a characteristic blue precipitate is formed. This is a co-ordination compound similar to those formed by nickel with dimethylglyoxime or by cobalt with nitroso-β-naphthol (q.v.).

6. Although magnesium oxalate is insoluble in water, there is practically no precipitate formed when *ammonium oxalate* solution is added to a solution of a magnesium salt.

DRY TEST

When heated with alkali carbonate on charcoal, magnesium salts leave a white incandescent oxide.

Potassium

There is a white normal oxide K_2O, hard to obtain pure, and a yellow peroxide K_2O_4. The potassium ion forms few insoluble compounds.

REACTIONS (*use a solution of potassium chloride*).

1. A freshly made solution of sodium cobaltinitrite in acetic acid gives a yellow precipitate with a solution containing potassium ions.

$$Na_3[Co(NO_2)_6]+2KCl = K_2Na[Co(NO_2)_6]+2NaCl.$$

2. Sodium hydrogen tartrate solution, in the presence of acetate ions to lower the acidity, gives a white precipitate of potassium hydrogen tartrate. The test is best carried out by adding to a concentrated solution of the suspected potassium salt on a watch-glass a few drops of concentrated sodium acetate solution (acidifying if necessary with the minimum quantity of acetic acid). If the tartrate is then added and the watch-glass scratched, the precipitate should form easily.

3. Sodium picrate solution in the presence of sodium carbonate gives a feathery yellow precipitate of potassium picrate.

Note that ammonium ions give precipitates with all these reagents and should therefore not be present when the above tests are made for potassium.

DRY TEST

Flame: Lilac; pink through 'cobalt' (blue) glass.

Sodium

The normal oxide is Na_2O (white) which is not easily obtained. There is a cream-yellow peroxide Na_2O_2 which is a derivative of hydrogen peroxide. The sodium ion forms extremely few insoluble compounds.

REACTION (*use a solution of sodium chloride*).

1. Boil a suspension of potassium pyroantimonate in potassium hydroxide solution and filter into a hot concentrated neutral or alkaline solution of the suspected sodium salt. Boil the mixed solutions and scratch the side of the test-tube with a glass rod if necessary. A granular precipitate of sodium pyroantimonate $Na_2H_2Sb_2O_7$ forms.

DRY TEST

Flame: intense and persistent golden yellow.

Detection of ammonium compounds

Although ammonium compounds give the reactions described under **Potassium**, the most satisfactory tests for these compounds are as follows:

1. Heating the substance with any alkali will liberate ammonia gas, recognizable by its smell and the fumes which it forms with hydrogen chloride, by the fact that it turns moist red litmus blue or turmeric paper brown, and that it is extremely soluble in water, or by reaction **2.**

2. Ammonia gas or a solution of an ammonium compound will give a brown precipitate with *Nessler's solution*, which is a solution containing mercuric iodide in alkaline potassium iodide, i.e. a solution of $K_2(HgI_4)$ in potassium hydroxide (cf. **Mercuric ion 1**). The precipitate has the empirical composition NHg_2IH_2O and has been formulated in various ways. A trace of ammonia gives a brown colour to the solution but no precipitate.

DRY TESTS

On heating, practically all ammonium compounds decompose into ammonia and a free acid. If the acid is volatile the vapours recombine to form a sublimate. Non-volatile acids may be left as residues, and oxidizing acids may liberate nitrogen or nitrous oxide by their action on the ammonia.

The Third Main Group: Summary

Except in the cases of sodium and potassium the differences in behaviour in this group are mostly small differences in degree of solubility rather than fundamental differences in character, and can best be understood by a fairly detailed comparative study of the group.

1. The **chlorides** and **iodides** are all soluble.

2. **Hydroxides.** The solubility of the hydroxides increases from that of magnesium hydroxide (about 2×10^{-4} gm.-mols. per litre) through calcium hydroxide (2×10^{-2} gm.-mols. per litre), strontium hydroxide, and barium hydroxide (0·2 gm.-mols. per litre) to sodium and potassium hydroxides which are very soluble indeed. Magnesium hydroxide is therefore precipitated by the addition of sodium hydroxide to a solution of a magnesium salt, but never completely precipitated by ammonium hydroxide. It is immediately dissolved by ammonium chloride solution which lowers the concentration of hydroxyl ion below 6×10^{-6} which is required by the solubility product of $Mg(OH)_2$ ($3{\cdot}4 \times 10^{-11}$) for precipitation from normal solutions of magnesium ion.

Calcium, strontium, and barium hydroxides are not completely precipitated even by sodium hydroxide, and not at all by ammonium hydroxide.

3. Sulphides. Those of magnesium, calcium, strontium, and barium are sparingly soluble; those of sodium and potassium are readily soluble. All are readily hydrolysed by water, but the hydroxides so formed are not precipitated in the presence of ammonium ions (see above).

4. Sulphates. Potassium, sodium, and magnesium sulphates are all very soluble. Calcium sulphate is sparingly soluble (2 gm./litre) and the sulphates of strontium and barium definitely 'insoluble' ($1{\cdot}1 \times 10^{-1}$ and $1{\cdot}1 \times 10^{-5}$ gm./litre, respectively). Dilute sulphuric acid will therefore give a precipitate with strontium and barium ions, but unless alcohol is added to lower the solubility, no precipitate is given with calcium ions in dilute solution. The concentration of the ions causing these precipitates can be lowered in two ways, both resulting in the redissolving of the precipitate.

(*a*) With all three cations a soluble acid salt can be formed in the presence of considerable excess of free acid.

(*b*) Complex ions of the type $[Ca(SO_4)_2]''$ are formed in the presence of considerable sulphate ion.

Either effect is readily noticeable in the case of calcium sulphate, which is soluble in concentrated acids or in a concentrated solution of ammonium sulphate. The less soluble strontium sulphate is soluble in hot concentrated hydrochloric acid or in concentrated sulphuric acid, but not in ammonium sulphate solution, whereas the very insoluble barium sulphate is appreciably soluble only in hot concentrated sulphuric acid.

5. Chromates. The solubility of the normal chromates increases in the same order as that of the sulphates, the magnesium salt being the most soluble, but in this case the barium salt alone shows marked insolubility ($3{\cdot}8 \times 10^{-3}$ gm./litre) and is the only one which is insoluble in acetic acid. Any appreciable concentration of hydrogen ion converts even this precipitate into the soluble dichromate. The solubilities of strontium and calcium chromates at 15° are about 1·2 and 23 gm./litre respectively. The dichromates are all soluble.

6. Carbonates. There is very little difference in the actual solubilities of barium, strontium, and calcium carbonates (about 1×10^{-2} gm./litre), but the variation in equivalent weight causes a slight increase, in the order mentioned, in the solubility products. Magnesium carbonate is rather more soluble ($4{\cdot}3 \times 10^{-1}$ gm./litre) and the carbonates of sodium and potassium are quite soluble.

The bicarbonates of all these cations are soluble, and free carbonic acid will therefore redissolve the precipitated carbonates of barium, strontium, calcium, or magnesium. Other acids eventually decompose the precipitates.

The lowering of the concentration of carbonate ions can be effected by the addition of excess ammonium ions, since ammonium carbonate is hydrolysed in solution; the free acid and free base formed by hydrolysis are both only slightly ionized and are readily decomposed.

$$CO_3'' + 2NH_4^{\cdot} \rightleftharpoons 2NH_3 + H_2O + CO_2.$$

Excess of ammonium ions, especially in hot solutions, tends therefore to dissolve the insoluble carbonates and the effect is more noticeable the more soluble the carbonate. Hence magnesium carbonate is readily soluble in cold ammonium chloride solution, calcium carbonate is appreciably soluble in this reagent, whereas strontium and barium carbonates require prolonged boiling with the ammonium chloride solution before they are redissolved (as chlorides).

7. The normal or tertiary **phosphates** and the secondary phosphates of barium, strontium, calcium, and magnesium are insoluble in water, but the primary salts, e.g. $Ca(H_2PO_4)_2$, are soluble. In the presence of sufficient hydrogen ion (dilute mineral acid), therefore, the phosphate precipitates are redissolved. The addition of free alkali, e.g. ammonium hydroxide, naturally displaces the equilibrium in favour of the normal salt by removal of hydrogen ion, but in the case of magnesium an insoluble 'double salt' magnesium ammonium phosphate $MgNH_4PO_4$ is precipitated. The precipitation of these phosphates in alkaline solution may interfere with the analysis of the second main group, and the removal of the phosphate ions from solution is sometimes necessary at that stage. The phosphates and acid phosphates of sodium and potassium are all soluble.

8. Oxalates. The solubility of the oxalates is in the reverse order to that of the carbonates and chromates so far as barium, strontium, and calcium are concerned. Barium oxalate (0·4 gm./litre) is soluble in hot dilute acetic acid; strontium oxalate ($6{\cdot}6 \times 10^{-2}$ gm./litre) is slightly soluble, and calcium oxalate (8×10^{-3} gm./litre) is quite insoluble in this reagent. Magnesium oxalate is insoluble in water, but soluble in acids or in ammonium oxalate solution. The alkali oxalates are soluble.

Non-ionic Reactions: Dry Tests

The reactions of a solid substance may depend upon the presence of certain anions or cations or on a particular combination of radicals. A great many of the tests which can be carried out with solid materials have been mentioned or implied in the sections descriptive of the anions and cations, but the tests commonly applied, whether relating to anions or cations are summarized below. Notes constructed from personal experience of the tests should be used in preference to the following which is only meant to serve as a guide.

A. The effect of heat on a substance

The substance should be placed in a small, hard-glass test-tube and heated with a Bunsen flame, at first slowly and then vigorously.

1. *Volatility* or *sublimation* in part or as a whole is associated as a rule with compounds of mercury, arsenic, and the ammonium ion, with free sulphur or with loosely combined sulphur, and the nature of the products will help to indicate which of these substances, if any, is involved. It must be remembered that there are other appreciably volatile substances, such as cadmium oxide, and that any conclusions from evidence of volatility should be well confirmed.

2. *Decomposition* on heating, and the nature of the decomposition products, particularly the volatile ones, usually give information about the anion of a salt, although the residue is often characteristic of the metal concerned. Thus, *as regards the anion*:

Oxygen is given off by salts of the halogen oxyacids, nitrates, peroxides, and a few other oxidizing anions.

Sulphur is liberated from some sulphides and from thiosulphates.

Sulphur dioxide is given off by bisulphites and some sulphites.

Nitrogen peroxide by some nitrates (all except the alkali nitrates).

Carbon dioxide by nearly all carbonates and by salts of some organic anions.

Water vapour is given off by hydrated salts, but also by many acid salts (e.g. bicarbonates, acid phosphates, &c.) and by organic compounds on decomposition.

A more detailed account of these effects is given on p. 194.

As regards the cation.

When they are decomposed by heat, i.e. when the anion is that of a relatively volatile acid, salts of *mercury* and *silver* usually leave the metal with some oxide.

Salts of other cations except those of the alkali metals are usually converted to oxides, but the ease of decomposition diminishes from compounds of cations of the first main group (Hg, Ag, As, Sb, Bi, Cu, Sn, Pb, Cd) through those of the second (Zn, Ni, Co, Fe, Mn, Cr, Al) to those which are decomposed only with difficulty (Mg, Ca, Sr, Ba). In particular the abnormal decomposition of alkali nitrates and the stability of alkali carbonates should be noted. This general order of stability is naturally the reverse of that which represents the susceptibility of the metals to attack by oxygen and acids (p. 78), and, in common with the behaviour of the sulphides and other characteristic compounds, is determined almost entirely by the positions of the metals concerned in the periodic table.

B. Charcoal Tests

A further elaboration of the tests described above consists in heating the powdered substance either alone or mixed with double its bulk of anhydrous sodium carbonate in a cavity scraped in a charcoal block. These tests help to identify substances by revealing the nature of their reduction products. 'Fusion mixture' (mixed sodium and potassium carbonates) can be used with advantage as it has a lower melting-point than sodium carbonate.

A mouth-blowpipe is usually used for heating the mixture. The jet of the blowpipe is directed into a flat, luminous, gas flame. This is obtained by dropping a flattened tube with a slanting top inside the tube of a Bunsen burner so that it covers the air inlet. By putting the jet of the blowpipe well inside the luminous flame at its base and blowing hard an excess of hot oxygen will be driven into the tip of the flame. This is called the *oxidizing flame.* By holding the jet at the edge of the flame and blowing gently a pointed luminous flame containing unburnt gases is formed and the tip of the yellow cone of this flame (not the extreme tip) is called the *reducing flame.*

1. *Heating the substance alone.* The tip of the oxidizing

flame is used. The main point to be noticed here, in addition to the normal decomposition of the substance, is that the presence of an oxidizing agent (e.g. oxyacids of the halogens and nitrogen) is shown by deflagration of the charcoal.

2. *Heating the substance with fusion mixture.* This should be done in the reducing flame. The primary reaction is an ordinary double decomposition with sodium carbonate. Sodium salts of the anions present and the carbonates of the cations are formed. The charcoal absorbs the molten alkali salts and reduces if possible the products formed by the high-temperature decomposition of the carbonates. The final products of reaction are therefore either metals alone, metals and their oxides, or oxides. Here again the behaviour of the metals concerned is determined by their positions in the periodic table and hence can be correlated with the analytical groups. The volatility of the reduced metals, however, imposes a secondary effect.

The oxides of the metals in the first main group are all easily reduced, those of silver and mercury being decomposed at the temperature of the blowpipe even in the oxidizing flame. In addition to these, the oxides of the neighbouring elements zinc, nickel, cobalt, and iron are all reduced fairly readily by carbon. Some of the metals concerned are non-volatile (and with the exception of tin these all lie together in the periodic table). These non-volatile metals show no sign of re-oxidation. Beads are formed by the lower-melting ones: *silver*, *copper*, and *tin* (all malleable). Fine particles are formed by the higher-melting ones: *iron*, *nickel*, and *cobalt* (all magnetic).

Of the remainder, *antimony*, *bismuth*, and *lead* are moderately volatile, and some of the metallic vapour is oxidized and deposited round the metal (Sb_2O_4 white, Bi_2O_3 yellow, PbO yellow). Bismuth and antimony are brittle; lead is malleable and soft enough to mark paper.

Arsenic, *zinc*, and *cadmium* are completely converted to the corresponding oxides owing to their greater volatility, so that no bead remains. As_2O_3 is white (with a smell of garlic when hot), ZnO is white (yellow when hot), and CdO is brown. *Mercury* is completely volatilized and not re-oxidized.

The carbonates of the remaining metals, except the alkali metals and barium, are decomposed to oxides by the mouth-blowpipe, but these oxides are not easily reduced. Of the oxides the white ones (MgO, CaO, SrO, Al_2O_3 and other 'earths') show incandescence when hot. If a white residue or white oxide incrustation is left on the charcoal block it may be treated with a drop of cobalt nitrate solution and again heated. A bright blue colour (*Thénard's blue*) indicates the presence of aluminium oxide and a pale green colour (*Rinmann's green*) indicates the presence of zinc oxide.

C. Borax Beads

A more important series of coloured compounds used as dry tests are the coloured borates formed by the transition metals in the middle of the long periods of the periodic table. When borax $Na_2B_4O_7\,10H_2O$ is heated it swells up until its water of crystallization has been given off, when it melts to a 'glass'. A bead of this borax glass can be formed by heating a platinum wire or glass rod, dipping it into borax, heating again and repeating this until enough borax has accumulated in the bead. If the bead is then dipped into a dilute solution of the substance for examination, or a *very small quantity* of the solid added, and the whole fused in a Bunsen or blowpipe until the bead is clear again, characteristic colours will develop on cooling if certain metals are present. The commonest of these are *chromium*, *manganese*, *iron*, *cobalt*, *nickel*, and *copper* (all adjacent to one another in the periodic table and all forming coloured ions). The colour of the bead can usually be changed by reheating the bead in a reducing flame, with the assistance if necessary of a little stannous chloride. The colours obtained are:

Metal	*Oxidizing flame*	*Reducing flame*
chromium	green	green
manganese	amethyst	colourless
iron	yellow or red (hot)	green
cobalt	blue	blue
nickel	brown	grey[1]
copper	green (hot), blue (cold)	red

D. Flame Tests

Whereas most of the dry tests described above are useful in connexion with the more noble metals of the first two main groups, colours imparted to non-luminous flames by various substances are chiefly due to metals in the third main group, as the production of a visible colour is connected to some extent with ease of ionization. The most volatile compounds available are best for showing characteristic flame tests, and in general the chlorides are the most serviceable. These are obtained by mixing a little of the unknown substance with a little moderately concentrated hydrochloric acid on a watch-glass and taking up a drop of the mixture on the end of a straight platinum wire or a loop of clean nickel wire; or better still on a clean nickel spatula. If the substance is held at the edge of the base of the flame the alkali halides, which are the most volatile, will if present colour the flame. On raising the wire above the hot tip of the inner cone the less volatile chlorides, e.g. those of the calcium group, are revealed. The colours which may be noticed are as follows:

Sodium: an intense and persistent golden yellow.

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[1] Several metals give a grey bead in the reducing flame owing to separation of the metal.

Potassium: a lilac-coloured flame. This cannot be seen in the presence of sodium except through 'cobalt' (blue) glass, when it appears pink.

Calcium: brick-red.

Strontium: bright red.

Barium: greenish yellow.

Of the less common elements *lithium* gives a bright red and *thallium* a bright green flame, while the very rare element *indium* colours the flame blue. *Copper* halides gives a green coloration and *antimony*, *tin*, and *lead* all give a bluish-white appearance to the flame. Free *boric acid* also imparts a green colour to the flame (see **Borates 2**).

IV

SUGGESTIONS FOR THE IDENTIFICATION OF A SINGLE SUBSTANCE

IN order to identify a single substance the student should construct for himself, from his knowledge of the reactions of the ions and elements concerned, a scheme of analysis which he should amplify with his own comments. The suggestions given here may be taken as a skeleton for such a scheme.

A 'single substance' may be a natural product or an industrial product, in which case it is almost certain to contain impurities; or it may be a carefully purified specimen in which case impurities are possible but unlikely. As many of the reactions used in analysis are very sensitive (e.g. the detection of sodium by the flame test or of iron by the Prussian blue reaction) the impurity may be mistaken for the main substance, but only those substances should be regarded as present which give substantial precipitates comparable in quantity with the material taken for analysis.

When the subject for analysis is known to be a single substance it is possible by the application of a series of preliminary tests (mainly the dry tests described on pp. 132–8) to obtain fairly definite evidence of its identity. It is largely a matter of opinion and judgement just how far these tests should be applied before a systematic analysis is carried out with the substance in solution. The main objections to their use are that they are not always conclusive, and, what is more important, they are not as a general rule exclusive. It is a good working rule that if a substance can be dissolved with ease in one of the usual solvents (see below) it is better to identify the substance by precipitation reactions. If a solution is difficult to obtain, then the dry tests will serve not only to indicate the nature of the substance, but also to indicate the best method of attacking it in order to get it into solution.

Before examining the solubility of the substance it is as well in all cases

(1) to make a critical inspection of the physical properties of the substance (colour, odour, crystalline form, approximate hardness and density should be noted);

(2) to examine the effect of heat on the substance, particular note being taken of its *changes of state or colour*, its *volatility*, and its *thermal stability*.

(3) to test for the presence of ammonium salts (**NH**$_4$ **1**)

Any conclusions which may be drawn from these observations (see p. 133) *should be written down immediately*.

The other dry tests can be applied at this point if desired, but deductions made from them should not be allowed to prejudice the observer. Do not try to make subsequent observations 'fit' erroneous deductions.

The problem now arises of making a solution for analysis which shall contain the ions to which the unknown substance will give rise. In the first place, the substance may be soluble in *water* in which case no difficulties arise. (How to test the solubility of a substance in a solvent is described below.) If the substance is insoluble in water, it may be, like calcium phosphate, the salt of a weak acid which (see p. 10) will dissolve in more highly dissociated acids; or, like calcium carbonate, the salt of an unstable acid, which is decomposed by more stable acids. As hydrochloric acid is to be used eventually for acidifying the solution, it is clear that if an acid is necessary to effect solution of the substance, *hydrochloric acid* is the most suitable. If the *dilute* acid is not sufficient for this purpose, the *concentrated* acid may serve. There are comparatively few substances which this acid does not dissolve or decompose.

Should it be necessary to go further, the oxidizing power of nitric acid, coupled with the more general solubility of its salts, makes it a more effective solvent, and there are cases (where solution in hydrochloric acid is not possible) where *dilute nitric acid* can be used with advantage without seriously inconveniencing the subsequent analysis. Concentrated nitric acid is to be avoided, as its oxidizing properties interfere with the normal action of the group reagents, particularly hydrogen sulphide. If the combination of a concentrated acid and an oxidizing agent is needed, *aqua regia* should be used. This is best obtained by suspending the substance for analysis in warm concentrated hydrochloric acid and dropping in concentrated nitric acid, with heating if necessary, until no further reaction with the substance occurs. This avoids an excess of nitric acid. The advantage of this solvent is that it constitutes a source of free chlorine (produced by the oxidation of the hydrochloric by the nitric acid) and the products of its action are chlorides, the salts most suited for analytical purposes. Excess chlorine and oxides of nitrogen should be removed by thorough boiling once the solution has been made; it should then be cooled and diluted.

A distinction must be made between *testing the solubility of a substance* in these solvents and *making up a solution for analysis*.

Testing the solubility of a substance

For this purpose it is absolutely imperative that there should be plenty of solvent available. This is best ensured by the following procedure. Take about 5 c.c. of water in a thoroughly clean test-tube, warm gently, and drop in *a few small particles* of the unknown substance. (It must be understood that here and wherever water for reagents is mentioned *distilled water* is implied.) If the substance does not at once disappear, apply heat. If the substance dissolves *and remains in solution on cooling* it may be considered soluble in water for the purposes of analysis. If all, or a part, of it remains undissolved the next solvent should be tried, until a suitable solvent has been found. After water the solvents tried should be, for reasons given above,

(i) dilute hydrochloric acid;
(ii) concentrated hydrochloric acid;
(iii) dilute nitric acid; and
(iv) aqua regia.

This order should be adhered to strictly, and the test carried out in each case as for water. If the substance proves to be insoluble in all the solvents named it should be examined in the way suggested on p. 157 (treatment of substances insoluble in aqua regia). Note that the liberation of chlorine from concentrated hydrochloric acid indicates that the unknown substance is an oxidizing agent, while the gaseous products, if any, evolved when dilute hydrochloric acid is used as a solvent should be identified in order to ascertain the anion responsible for them.

Making a solution

The ease with which the substance dissolved in the solubility tests must guide the analyst in making up his solution for analysis. It should always be remembered that the tests used are, on the whole, very sensitive, and only a small quantity of material is necessary to give positive results. On the other hand very dilute solutions should be avoided. Any gases formed during the solution of the substance must be carefully expelled by boiling, otherwise they will interfere with the subsequent tests. Solutions made in water should be tested immediately for acidity or alkalinity. Less than one gram of material should suffice for a complete analysis for the cation, but it is sometimes convenient to dissolve a larger quantity if available in order to have a reserve of the original solution.

Scheme of analysis for cations

The principles of cation analysis have been discussed on p. 13 et seq. and their application to simple salt analysis on p. 23. Only the experimental procedure is outlined below. The solution of the unknown substance will be referred to as the *original solution* (O.S.).

I. To a portion of this solution add dilute hydrochloric acid a few drops at a time until precipitation, if any, is complete. If the solution has been made in dilute hydrochloric acid this step is still advisable, as the acid may have been used up in dissolving the substance and a definitely acidic solution is required for the next step. If the solution has been made in concentrated hydrochloric acid or aqua regia it should be diluted. Precipitates of bismuth or antimony oxychlorides may appear in this case (**Bi 6** and **Sb 1**), but they will redissolve with a *little* concentrated hydrochloric acid, and in any case will not answer to the confirmatory tests for the cations of Group I.

If a precipitate forms on the addition of hydrochloric acid it normally consists of the chloride of one of the cations **silver ($Ag^{\cdot}$)**, **lead ($Pb^{\cdot\cdot}$)**, or the **mercurous ion ($Hg_2^{\cdot\cdot}$)**

To distinguish between the Group I cations, all of whose chlorides are colourless

Its solubility in hot water distinguishes lead chloride from the other two. If, therefore, the precipitate is allowed to settle (shaking and warming *gently* will help it to settle quickly), the liquid above it decanted, and distilled water added and boiled, two things may occur:

(*a*) *The precipitate dissolves.*

It may recrystallize on cooling, in which case it is almost certainly lead chloride. For confirmation, precipitate any other characteristic insoluble lead salt, e.g.

1. To O.S. add potassium iodide solution: a yellow precipitate of lead iodide PbI_2 forms, soluble in hot water, giving a *colourless* solution as both ions are colourless; recrystallizing in glistening yellow hexagonal plates (**Pb 2**).

2. To O.S. add hydrogen sulphide; decant the liquid and shake the precipitated lead sulphide (PbS: black) with H_2O_2. White lead sulphate ($PbSO_4$) is formed (**Pb 4**).

3. To O.S. add potassium chromate solution. A yellow precipitate of lead chromate ($PbCrO_4$) forms which is converted to a red basic lead chromate $PbCrO_4 Pb(OH)_2$ on warming with lime water (**Pb 6**).

(*b*) *The precipitate does not dissolve.*

The effect of ammonium hydroxide solution will then differentiate between the other two cations, for silver chloride is soluble in this reagent, whereas mercurous chloride is turned black by it (**Ag 1** and **7**, and **$Hg_2^{\cdot\cdot}$ 1**).

For confirmation the characteristic precipitates with potassium iodide and potassium chromate can again be used in each case, the formation of a silver mirror by reduction being a useful additional confirmation for silver (**Ag 2, 6,** and **8; $Hg_2^{\cdot\cdot}$2** and **7**).

II. If the addition of hydrochloric acid has produced no precipitate the solution is ready for the addition of hydrogen sulphide. This may be added either as a saturated solution of the gas in water or by passing the gas itself through the acidified solution. It is important to add the reagent *very gradually* at first, noting *all* colour changes, but also to make sure eventually that the hydrogen sulphide is there in large excess. A precipitate at this stage indicates the presence of one of the Group II cations whose sulphides are characterized to some extent by their colour.

Dark coloured precipitates are given by the **mercuric** (**Hg**$^{\cdot\cdot}$), **copper** (**Cu**$^{\cdot\cdot}$), **bismuth** (**Bi**$^{\cdot\cdot\cdot}$), and **stannous** (**Sn**$^{\cdot\cdot}$) ions.

An orange precipitate is given by **antimony** (**Sb**$^{\cdot\cdot\cdot}$).

Yellow precipitates are given by the **stannic** (**Sn**$^{\cdot\cdot\cdot\cdot}$), **arsenic** (**As**$^{\cdot\cdot\cdot}$), and **cadmium** (**Cd**$^{\cdot\cdot}$) ions.

If hydrogen sulphide is added cautiously the black HgS precipitate is preceded by a white precipitate (chlorosulphide) which gradually darkens in colour to yellow, then brown and finally black.

To distinguish between the Group II cations

Of the *dark coloured* precipitates only stannous sulphide (SnS) is soluble in yellow ammonium sulphide. Confirm in O.S. by the action of sodium hydroxide or mercuric chloride (**Sn**$^{\cdot\cdot}$ **2** and **5**). Copper sulphide (CuS) and bismuth sulphide (Bi_2S_3) are insoluble in yellow ammonium sulphide, but unlike mercuric sulphide (HgS) they are soluble in nitric acid (1:1). The action of ammonium hydroxide on the original solution distinguishes between these two (**Cu 3** and **Bi 3**). Confirm copper in O.S. by the action of sodium hydroxide or potassium ferrocyanide (**Cu 2** and **6**) and bismuth by the precipitation of the oxychloride or the reaction with potassium iodide (**Bi 1** and **6**).

If the dark coloured precipitate is insoluble both in yellow ammonium sulphide and in nitric acid, then confirm mercury in O.S. by the action of potassium iodide or stannous chloride (**Hg**$^{\cdot\cdot}$ **1** and **6**).

For the *orange*-coloured precipitate (antimony sulphide Sb_2S_3) which is soluble in yellow ammonium sulphide, confirm antimony in O.S. by the action of water, sodium hydroxide, or sodium thiosulphate (**Sb 1, 3,** and **6**).

Of the *yellow* precipitates, yellow ammonium sulphide dissolves arsenic sulphide (As_2S_3) and stannic sulphide (SnS_2), but not cadmium sulphide (CdS). For the soluble precipitates add ammonium hydroxide to the O.S. Stannic ions give a white precipitate; arsenic gives none. Confirm arsenic in O.S. by the precipitation of Scheele's green (**As 5**) and stannic tin by the action of sodium hydroxide (**Sn**$^{\cdot\cdot\cdot\cdot}$ **2**). For the insoluble precipitate confirm cadmium in O.S. by the action of sodium and ammonium hydroxides (**Cd 1** and **2**). Note that (*a*) the colour of the sulphide precipitate, (*b*) its solubility in yellow ammonium sulphide, and (*c*) its solubility in nitric acid, together with the action of ammonium hydroxide on the original solution, serve to identify the cations of this group. Confirmatory tests should be applied.

Even if there is no precipitate there may be colour changes on the addition of hydrogen sulphide, accompanied by milkiness in the solution due to the formation of finely divided sulphur. These changes are caused by the reducing action of hydrogen sulphide and the two most common are:

(i) A change from orange to green due to the reduction of chromates in acid solution (dichromates) according to the equation:

$$Cr_2O_7'' + 8H^{\cdot} + 3H_2S = 2Cr^{\cdot\cdot\cdot} + 7H_2O + 3S.$$

(ii) A change from a yellow to a practically colourless solution due to the reduction of ferric to ferrous ions:

$$2Fe^{\cdot\cdot\cdot} + H_2S = 2Fe^{\cdot\cdot} + 2H^{\cdot} + S.$$

III. If there should be no precipitate with hydrogen sulphide in acid solution tests are made for sulphides which are insoluble in alkaline solution or which are hydrolysed to *insoluble* hydroxides. To obviate the necessity of boiling the solution until it is free from hydrogen sulphide, and to avoid reduction changes, take a *fresh* sample of the original solution, add an equal quantity of ammonium chloride solution, and then add ammonium hydroxide until alkaline. In the event of a precipitate forming the ammonium hydroxide must be added until precipitation is complete. *Whether there is a precipitate or not at this stage*, continue by adding hydrogen sulphide, in solution or as a gas, until there is no further change apparent. The character of the precipitates which may form can be seen from the appropriate experiments described on pp. 104–18, but for convenience they are tabulated below.

The addition of sodium hydroxide to the original solution, followed by excess of the same reagent, with boiling, will further differentiate between the cations of this group. The addition of hydrogen peroxide to the alkaline solution (with any precipitates it may contain) will complete the identification. The results of these tests are also tabulated.

Further confirmation of the presence of these ions may be obtained by the following tests on the original solution.

Zinc by the action of potassium ferrocyanide (**Zn 6**).

Nickel by the action of dimethylglyoxime (**Ni 5**).

Cobalt by precipitation as potassium cobaltinitrite or by the action of nitroso-β-naphthol or ammonium thiocyanate (**Co 5, 6,** and **7**).

Ferrous ion by the action of potassium ferricyanide (**Fe$^{\cdot\cdot}$ 6**).

Ferric ion by the action of potassium ferrocyanide or ammonium thiocyanate (**Fe$^{\cdot\cdot\cdot}$ 6** and **7**).

Manganese by permanganate formation with red lead and nitric acid (**Mn 5**).

A. Characteristic reactions of Group III cations

Ion	*Effect of adding ammonium chloride solution, followed by ammonium hydroxide*	*Effect of then adding hydrogen sulphide*
Zinc $Zn^{\cdot\cdot}$	——	White ppt. ZnS
Nickel $Ni^{\cdot\cdot}$	Solution changes colour on addition of NH_4OH from green of $Ni^{\cdot\cdot}$ to blue of $[Ni(NH_3)_6]^{\cdot\cdot}$	Black ppt. NiS
Cobalt $Co^{\cdot\cdot}$	Slight colour change on adding NH_4OH (pink of $Co^{\cdot\cdot}$ to brown of $[Co(NH_3)_6]^{\cdot\cdot}$)	Black ppt. CoS
Ferrous $Fe^{\cdot\cdot}$	Dirty greenish-white ppt.	Ppt. changes to black FeS
Ferric $Fe^{\cdot\cdot\cdot}$	Red-brown ppt. $Fe(OH)_3$	Ppt. changes to black Fe_2S_3
Manganese $Mn^{\cdot\cdot}$	A slight trace of a brown ppt. may form	Flesh-coloured ppt. MnS
Chromium $Cr^{\cdot\cdot\cdot}$	Dull green precipitate $Cr(OH)_3$	No change
Aluminium $Al^{\cdot\cdot\cdot}$	White gelatinous ppt. $Al(OH)_3$	No change

B. Further characteristic reactions of Group III cations

Ion	*Effect of adding sodium hydroxide*	*Effect of adding excess* NaOH	*Effect of boiling* NaOH *solution*	*Effect of hydrogen peroxide on* NaOH *solution*
Zinc $Zn^{\cdot\cdot}$	White ppt. $Zn(OH)_2$	Ppt. dissolves. Soln. gives white ppt. ZnS with H_2S; none with NH_4Cl	No change	No change
Nickel $Ni^{\cdot\cdot}$	Green ppt. $Ni(OH)_2$	No change	No change	No change
Cobalt $Co^{\cdot\cdot}$	Blue ppt. (basic salt)	Ppt. changes to pink $Co(OH)_2$	Slight darkening in air	Ppt. changes to dark-coloured $Co(OH)_3$
Ferrous $Fe^{\cdot\cdot}$	Dirty green ppt. turning dark	No change	Darkens in air	Ppt. changes to red-brown $Fe(OH)_3$
Ferric $Fe^{\cdot\cdot\cdot}$	Red-brown ppt. $Fe(OH)_3$	No change	No change	No change
Manganese $Mn^{\cdot\cdot}$	White ppt. $Mn(OH)_2$	No change	Darkens in air	Ppt. changes to dark brown hydrated MnO_2
Chromium $Cr^{\cdot\cdot\cdot}$	Dull green ppt. $Cr(OH)_3$	Ppt. dissolves	Re-pptn. of basic chromite	Yellow solution of Na_2CrO_4 formed. Confirm by perchromate test (**Chromates 4**)
Aluminium $Al^{\cdot\cdot\cdot}$	White ppt. $Al(OH)_3$	Ppt. dissolves. Soln. gives no ppt. with H_2S but white ppt. $Al(OH)_3$ with NH_4Cl	No change	No change

Chromium by reduction with zinc and precipitation of chromous acetate (**Cr 5**).

Aluminium. No further tests on O.S. Formation of Thénard's blue on charcoal can be used.

Borax bead tests can be used for *nickel*, *cobalt*, *iron*, *manganese*, and *chromium*, and the formation of Rinmann's green on charcoal for *zinc*.

Should colourless precipitates be formed by the action of ammonium hydroxide, and by the action of sodium hydroxide, which are *not soluble* in excess of sodium hydroxide solution, they indicate that a substance is present which is soluble in acid, but insoluble in alkaline or neutral solutions. Such substances are usually phosphates or oxalates of the elements calcium, strontium, barium, or magnesium. The presence of a phosphate or oxalate should be confirmed, e.g. by the ammonium molybdate test for phosphates (**Phosphates 4**) and by the action of concentrated sulphuric acid on the dry salt, or by the reduction of potassium permanganate solution for oxalates (**Organic acids 2** and **7**). Tests should then be made for the cations present as outlined below (p. 151).

IV. Assuming that phosphates or precipitates of a similar character have not interfered with the Group III reactions, and no ordinary group precipitate has been obtained, tests must be made for the remaining cations (calcium, strontium, barium, magnesium, sodium, potassium, and ammonium), whose sulphides are soluble in water or hydrolysed giving rise to appreciably soluble hydroxides. A portion of the *original solution* should again be made alkaline with ammonium hydroxide in the presence of ammonium chloride as before, but instead of hydrogen sulphide ammonium carbonate solution should be added. This will precipitate the carbonates of **calcium, strontium,** or **barium.** (Magnesium carbonate, though insoluble in water is soluble in ammonium chloride solution (see **Mg 3**).) By dissolving the precipitated carbonates in acetic acid and making use, *in this order*, of (i) the insolubility of barium chromate in this acid (**Ba 3**), (ii) the precipitation of strontium sulphate by a concentrated solution of ammonium sulphate or better its slow precipitation by calcium sulphate (**Sr 2** and cf. **Ca 2**), and (iii) the precipitation of calcium oxalate by ammonium oxalate solution (**Ca 6**), these three cations may be identified. They may be confirmed in the original solution as follows:

Barium by the action of sulphuric acid or calcium sulphate (**Ba 2**).

Strontium by the action of ammonium oxalate (**Sr 6**).

Calcium by the action of dilute sulphuric acid and alcohol (**Ca 2**).

Flame tests may be applied in each case.

Identification of phosphates, &c., of the calcium group

If there is a precipitate such as calcium phosphate in the third group, the test for cations must be made in hydrochloric acid solution. The addition of calcium sulphate solution will give an immediate precipitate of barium sulphate ($BaSO_4$) in the case of barium (**Ba 2**) and a slow-forming precipitate in the case of strontium (**Sr 2**). If neither of these cations is present, the addition of dilute sulphuric acid to the original solution, followed by an equal volume of ethyl alcohol, will cause a precipitate of calcium sulphate ($CaSO_4$) should calcium be present. If none of these three ions appear to be the cation of the salt, it is probably a magnesium compound, and a sodium carbonate extraction must be used to obtain the magnesium in a soluble form. The usual phosphate test can then be applied (**Mg 4**).

For this extraction the original substance is heated in a beaker with a boiling, saturated solution of sodium carbonate (with excess carbonate present). The solution is filtered off and will contain the sodium salt of the anion plus sodium carbonate. The residue should be decomposed with dilute hydrochloric acid when some of the magnesium now present as carbonate will be converted to the soluble chloride. This solution is also filtered off and used for identification of the cation.

V. If alkaline ammonium carbonate solution fails to give a precipitate, a fresh portion of the original solution should be made alkaline with ammonium chloride and ammonium hydroxide and a solution of sodium phosphate added. A white precipitate of magnesium ammonium phosphate ($MgNH_4PO_4$) will form if **magnesium** be present (**Mg 4**). The presence of this ion may be confirmed in the original solution by the action of sodium hydroxide and of ammonium carbonate (**Mg 1** and **3**).

In the absence of magnesium, separate portions of the original solution should be tested for:

- (i) **Ammonium** ion (if not already done) by heating the dry substance with lime (**NH_4 1**).
- (ii) **Potassium** by the action of sodium cobaltinitrite, sodium hydrogen tartrate, or sodium picrate (**K 1, 2,** and **3**). *These reactions are also given by ammonium compounds.*
- (iii) **Sodium** by the action of potassium antimonate (**Na 1**). Sodium and potassium may be confirmed by flame tests.

Identification of the anion of a single substance

When only one anion is present in a substance it is a comparatively simple matter to identify it, although the separation of anions is often extremely difficult. The most direct method of investigation is outlined below.

1. The effect of heat on the dry substance can give valuable but not necessarily conclusive information. The usual volatile products which may be identified are:

Oxygen: from salts of oxyacids of the halogens (e.g.

chlorates) from peroxides and 'per-salts', and from alkali nitrates.

Non-metallic oxides (which may or may not be mixed with oxygen): e.g.

Sulphur trioxide fumes from some sulphates.

Sulphur dioxide from heavy metal sulphites and sulphates, from sulphides in the presence of air, and possibly from thiosulphates.

Nitrous oxide from ammonium nitrate.

Nitrogen peroxide from heavy metal nitrites and nitrates. (Solid nitrites other than those of the alkali metals are uncommon.)

Carbon dioxide from heavy metal carbonates and organic compounds.

Elements, hydrides, &c., e.g.

Nitrogen from ammonium nitrite or dichromate.

Sulphur from thiosulphates.

Cyanogen $(CN)_2$ from various cyanogen compounds.

Phosphine from phosphites and hypophosphites.

Inflammable vapours from salts of organic acids.

Water vapour or *free acids* from hydrated or acid salts, e.g. H_2O and CO_2 from bicarbonates; HCl from $AlCl_3\,6H_2O$.

Absence of volatile products is usually associated with salts of an alkali or alkaline earth metal, or of a stable non-volatile acid, e.g. phosphates, borates.

2. The effect of **cold dilute hydrochloric acid** on the dry substance reveals salts of those acids which are less dissociated (weaker) in solution than hydrochloric acid and at the same time are very volatile, or are unstable and yield gaseous decomposition products. The equilibrium amounts in the equation

$$MA+HCl \rightleftharpoons MCl+HA$$

are thus shifted in favour of the right-hand side. As hydrochloric acid is usually added to the dry salt or its solution in water at an early stage in the analysis for cations, the anion is often identified incidentally in this manner.

The following anions are thus identified by the evolution of:

Chlorine: hypochlorites.

Hydrogen sulphide: all sulphides except those precipitated in dilute hydrochloric acid solution. Some of these will dissolve in more concentrated acid and will have revealed themselves as sulphides accordingly.

Sulphur dioxide: sulphites (more noticeable on warming).

Sulphur dioxide with liberation of sulphur: thiosulphates.

Nitric oxide mixed with *nitrogen peroxide*: nitrites.

Carbon dioxide: carbonates (and cyanates).

Hydrocyanic acid vapour: cyanides.

If on warming the solution *chlorine* is evolved there is an oxidizing agent present. If in addition *chlorine peroxide* is formed the salt is a chlorate (a bromate would give a mixture of chlorine and bromine). These reactions are more noticeable with moderately concentrated hydrochloric acid.

The properties and methods of manipulation and testing of the gases given off here or in other tests are summarized on pp. 25–30, or under the appropriate anions, and should be carefully studied. The student must satisfy himself that he can recognize satisfactorily the products of a known substance by the tests described. The anions mentioned above should be confirmed in solution if possible by the following reactions:

Hypochlorites: by the action of cobalt nitrate (**ClO' 3**).

Sulphides: by the action of tin and hydrochloric acid (**S'' 3**).

Sulphites: by their reducing action on potassium permanganate or dichromate (**SO_3'' 4** and **5**).

Thiosulphates: by the action of silver nitrate (**S_2O_3'' 3**).

Nitrites: by the action of ferrous sulphate in acetic acid (**NO_2' 4**).

Carbonates (if soluble): by the barium and silver precipitates (**CO_3'' 2** and **3**). (This will distinguish cyanates which are very uncommon, as barium cyanate is soluble.)

Cyanides: by the formation of a ferrocyanide and then Prussian blue (**Cyanogen group 8**).

3. The effect of **hot concentrated sulphuric acid** on the dry salt, if dilute hydrochloric acid has produced no effect, will help to identify nearly all the remaining common anions. Acids which are more volatile than this reagent or decomposed by it to give volatile products show positive results. The gaseous products which may be evolved are:

Hydrogen chloride: from chlorides (see note **Halides 2**). Confirm by oxidation to chlorine (**Halides 3**).

Hydrogen bromide and bromine: from bromides
Hydrogen iodide and iodine: from iodides
confirm by the action of silver nitrate or chlorine water (**Halides 7** and **8**).

Hydrogen fluoride: from fluorides. Confirm by the formation of silicon tetrafluoride (**Halides 5**).

Chlorine peroxide: from chlorates. This explodes on warming. Confirm by reduction to chloride (**ClO_3' 8**).

Bromine: from bromates: these are rather uncommon.

Sulphur dioxide: may be liberated by any reducing agent e.g. free metals, insoluble sulphides, carbon and organic matter, hypophosphites, &c.

Nitric acid vapour and nitrogen peroxide: from nitrates. Confirm by brown ring or reduction to ammonia (**NO_3' 4** and **5**).

Carbon monoxide: from (cyanides and) complex cyanides. Confirm by ferric chloride and ferrous sulphate (**Cyanogen group 6**). Also from formates: confirmed by reduction of silver nitrate or action of ferric chloride (**Organic acids 6** and **5**).

Carbon oxysulphide: from thiocyanates. Confirm with ferric chloride (**Cyanogen group 6**).

Carbon monoxide and carbon dioxide: from oxalates and tartrates. The latter will also char. Confirm oxalates by reduction of potassium permanganate and tartrates by formation of silver mirror (**Organic acids 7** and **8**).

Acetic acid vapour: from acetates (ethyl acetate test).

Manganese heptoxide: from permanganates. Violet coloured and explosive. Confirm by alkaline reduction to green manganate (**MnO_4' 5**).

4. The anions whose salts do not give positive results with either of these acid reagents include the perchlorate, iodate, sulphate, phosphate, arsenate, borate, and chromate ions, and to the salts of these must be added oxides and free elements. The most commonly occurring are sulphates, phosphates, and borates.

Sulphates may be identified by the addition of barium nitrate solution to a solution of the substance in dilute nitric acid (**SO_4'' 3**).

Phosphates by the ammonium molybdate test (**PO_4''' 4**).

Borates by the turmeric test or the methyl borate flame (**BO_2' 5** and **2**).

Arsenates and *chromates* will have given a clue to their identity in the analysis for cations (*slow* precipitation of As_2S_3 and reduction of chromates by hydrogen sulphide). They may be confirmed by the silver precipitate or molybdate test for arsenates (**AsO_4''' 3** and **4**) and the perchromic acid test for chromates (**CrO_4'' 4**).

Iodates may be recognized by the liberation of iodine by the action of a little sulphur dioxide (**IO_3' 8**).

Perchlorates give off oxygen on heating, leaving a chloride residue, but are not reduced by ferrous sulphate (**ClO_4' 1** and **3**).

If none of these anions appear to be present the substance is probably an oxide or free element. The 'cation' being known, it should be easy to verify this by comparison with known substances. Confirmation of anions by the character of the barium, calcium, or silver precipitates is always useful where possible.

The student should make up for himself a detailed scheme of analysis for a single substance based on that given above and incorporating the appropriate tests.

Treatment of substances insoluble in aqua regia

Substances which do not go into solution when treated with water or the usual acid solvents are limited in number, the more common of these being:

(*a*) the elements **carbon** and **sulphur**;

(*b*) the naturally occurring or ignited oxides of **aluminium (Al_2O_3)**, **chromium (Cr_2O_3)**, **tin (SnO_2)**, **silicon (SiO_2)**, and **antimony (Sb_2O_4)**;

(*c*) the **chloride, bromide, iodide**, and **cyanide** of **silver**; the **sulphates** of **barium, strontium**, and **lead**; naturally occurring **calcium fluoride** (fluor-spar) and **Prussian blue.**

Colour

Most of these are colourless but the colours of Prussian blue, carbon (black), sulphur (yellow), and chromic oxide (green) are characteristic. Silver iodide is pale yellow. Naturally occurring products are always liable to be coloured by almost undetectable traces of impurity, but the colour is hardly noticeable after grinding. (Typical colours are $SrSO_4$ ('celestine') blue; CaF_2 ('fluor-spar') purple, green, or iridescent; Al_2O_3 various colours, e.g. ruby, sapphire, amethyst; SiO_2 (silica, quartz, sand, opal, &c.) grey, yellow, pink, opalescent.

Effect of heat

Sulphur melts to a yellow liquid, darkens and becomes more viscous owing to molecular changes in the liquid, eventually becomes lighter in colour and more mobile, and after volatilizing burns with a blue flame with the production of sulphur dioxide. *Confirmation*: solubility in carbon bisulphide or toluene.

Carbon will also burn in air, but combustion can be made considerably more vigorous by adding the carbon in *very small quantities* to a little molten potassium nitrate in an iron spoon. The residue will be mainly potassium carbonate and will give off carbon dioxide on treatment with acids. *Confirmation*: on heating carbon with cupric oxide, red metallic copper is formed and carbon dioxide is evolved. The carbon reduces the copper according to the equation

$$C+2CuO = 2Cu+CO_2.$$

Of the *oxides*, stannic oxide turns yellow while hot and antimony oxide Sb_2O_4 melts to a yellow liquid, while the *salts*, silver chloride, silver bromide, and silver iodide, melt without further change. Silver cyanide, however, is decomposed by heat leaving a residue of metallic silver and giving off cyanogen gas. *Confirmation of* AgCN: dissolve residue in dilute nitric acid and apply **Ag 1** or **6**.

The character of those of the above compounds which are affected by heat may be further defined by **heating them with sodium carbonate on charcoal**, in which case the following results may be observed:

(i) *Stannic oxide* gives a white malleable bead soluble in hydrochloric acid, but not giving a clear solution with nitric acid.

(ii) *Antimony oxide* gives a brittle bead soluble in aqua regia, with a white incrustation.

(iii) The *silver salts* give a malleable bead soluble in nitric acid, but not in hydrochloric acid.

In addition to these substances, *lead sulphate* will give a malleable bead soluble in nitric acid, with a yellow incrustation.

Prussian blue may leave a grey powder (iron) soluble in hydrochloric acid. The solutions made by dissolving these beads in acid can be used to identify the metal by the ordinary cation reactions. If the substance remains as a white powder, addition of cobalt nitrate and further ignition should reveal the presence of any *aluminium oxide* by the formation of Thénard's blue.

Absence of any positive results in the above tests indicates that the substance is probably *silica* (white), *chromic oxide* (green), *barium sulphate* (white), *strontium sulphate* (white), *calcium fluoride* (white), or *Prussian blue.* The following characteristics serve to differentiate these substances.

Chromic oxide, which is green, will impart a green colour to a borax bead in the oxidizing or in the reducing flame, and on fusion with sodium peroxide in a nickel or iron crucible will give a yellow melt of sodium chromate which can be extracted *when cool* with water, and verified as such.

Caution: sodium peroxide should be handled with great care **and must not be put on paper or left on the bench.**

Prussian blue on treatment with concentrated sulphuric acid gives the reactions of a ferrocyanide (evolution of CO) and gives the characteristic iron colours to a borax bead. Boiling with sodium hydroxide solution gives a solution of sodium ferrocyanide and a residue of ferric hydroxide which are easily confirmed by the precipitation of copper ferrocyanide (**Cu 6**) and the thiocyanate test (**Fe**$^{\cdots}$ **7**) respectively.

Calcium fluoride on treatment with concentrated sulphuric acid gives off hydrogen fluoride which etches the containing vessel. The calcium can be brought into solution best by carrying out a sodium carbonate extraction on the residue. The formation of silicon tetrafluoride can also be used as a confirmation (**Halides 5**).

Barium and *strontium sulphates*, when heated with anhydrous sodium carbonate and powdered charcoal, form the corresponding sulphides which can be extracted with dilute hydrochloric acid. Hydrogen sulphide is given off and, after filtering, the solution gives the appropriate flame coloration and the cationic reactions for the metals. The reduction can be carried out very effectively on the end of a carbonized splint impregnated with fused washing soda.

Silica is best identified by the formation of silicon fluoride and its subsequent hydrolysis (**Silicates 2**).

The substance most likely to be confused with silica is aluminium oxide. This will not give the fluoride reaction, and may further be distinguished by (*a*) its solubility in molten potassium hydrogen sulphate, (*b*) its solubility in a bead of microcosmic salt formed on a platinum wire. Silica will not dissolve in the former or form a clear bead with the latter.

Making a 'solution'

If the above tests suggest the presence of a *salt* (e.g. $BaSO_4$), the substance should be fused with sodium carbonate or boiled with concentrated sodium carbonate solution. The aqueous extract should be filtered and neutralized exactly with dilute nitric acid. It can then be used for the normal tests for anions. The residue should be extracted with dilute nitric acid, and the filtrate examined for the suspected cation.

If solutions are required containing the anions of the insoluble *silver salts* they can be obtained by the use of zinc and sulphuric acid (**Halides 7**), the metallic residue being dissolved in nitric acid and tested for silver.

The *oxides* of aluminium and silicon usually yield to alkali fusion, and chromic oxide to a sodium peroxide fusion, but natural tinstone must first be converted to the sulphide and thence to the soluble sodium thiostannate, by heating with sodium carbonate and sulphur. The oxides of tin and antimony can also be reduced to the metal, which can then be treated with hydrochloric acid. Alumina can be attacked by an acid sulphate fusion.

V

DISCUSSION OF THE ANALYSIS OF A MIXTURE OF SUBSTANCES

EVERY substance requiring analysis is a problem in itself, and no hard and fast rules will ever serve to accommodate all cases. Apart from the actual investigation of unknown substances, the value of qualitative analytical exercises lies in the demand they make upon the powers of observation, deduction, and manipulation, and upon one's ingenuity in handling a difficult situation. The student should make his own scheme of procedure and annotate it according to his own experience. The following is a guide not an oracle.

As in the case of a single substance a mixture may be (*a*) a naturally occurring substance (usually called a 'mineral'), (*b*) an industrial product, or (*c*) an artificial mixture.

(*a*) The identification of the main constituents of a *mineral* is usually simple from a chemical standpoint once the substance has been converted into soluble compounds. (Minerals should always be very finely pulverized before the analysis is attempted.) In addition it should be remembered that naturally occurring anions are relatively few and that the common minerals are usually oxides, sulphides, carbonates, silicates, or phosphates, while sulphates, fluorides, chlorides, nitrates, and borates are also found in reasonable abundance.

(*b*) In dealing with an *industrial product* it is essential to bear in mind the conditions of its formation. Likely impurities will be (i) substances contaminating the source; (ii) substances introduced intentionally as reagents during manufacture, usually compounds of sodium, potassium, calcium, iron, or the common mineral acids; (iii) by-products; for example, commercial potassium perchlorate is unlikely to be free from either chlorate or chloride. The analyst should therefore correlate what he knows of the occurrence and the manufacture of substances with his analytical evidence.

(*c*) *Artificial mixtures.* These may be made up as a test of manipulative skill, or of chemical ingenuity, or without any particular reason at all. Unless they bear some relation either to natural or industrial products or to the reagents in some theoretical problem, or else serve to illustrate some definite chemical point or principle they are educationally of little value and are to be avoided. It is possible to concoct mixtures which successfully defy ordinary analytical procedure except at the expense of unlimited time and material. Such mixtures are best left alone.

To one who has been well trained in the identification of single substances there is nothing surprisingly new in the analysis of mixtures. The substance should be subjected to as detailed a preliminary investigation *as is consistent with economy of time.* The extent of this will vary with the facility acquired in carrying out, and the confidence consequently placed in, the dry tests given on pp. 132–8. The systematic analysis relies upon the reactive independence of ions in solution and involves the same 'group reagents' as are used in the case of a single substance.

The Preliminary Investigation

In dealing with a single substance the dry tests are as likely as not to give a fair indication of what to expect in the systematic analysis. In the case of mixtures it is as a rule most advantageous for these reactions to be used as confirmatory tests on precipitates which should contain one significant anion or cation only. This avoids the possible interference of two or more dry-test results with one another, limits the number of such tests which need actually be carried out with any given analytical subject, and gives the investigator a definite result to look for. As in the case of a single substance, however, it is useful to observe the **effect of heat** on the substance (cf. pp. 133, 152 and 194–6), although naturally little will be seen in the case of most minerals or high-temperature industrial products. *Everything noted should be written down immediately on observation.* Useful information can also be obtained at this point by carrying out the preliminary tests for anions; first, the treatment of a portion of the substance with dilute hydrochloric acid, warm if necessary, then, of another with (hot) concentrated sulphuric acid. The possible results of these tests are indicated on pp. 153–6 and discussed in more detail under the identification of anions (p. 198). The information they give may help considerably in explaining any abnormal results which occur in the main course of the analysis. In particular, if the effect of heat, and, more definitely, the evolution of carbon monoxide on treatment with concentrated sulphuric acid, indicates that an organic anion or a cyanide, simple or complex, is present, it is best to ignite the mixture gently before preparing a solution for cation analysis. This avoids considerable interference with the normal procedure at a later stage.

As a great many of the tests employed later are affected by the presence of ammonium ions, it is advisable to ascertain at this stage by the lime test (**NH_4 1**) whether ammonium compounds are present in quantity or not. It is then as well to proceed immediately to **examine the solubility** (*not* to make a solution: see p. 141) of the mixture in the usual solvents in the order, water, dilute hydrochloric acid, concentrated hydrochloric acid, dilute nitric acid, aqua regia, until an effective solvent is found.

(For details of manipulation see pp. 141–2.) Should none of these be effective the substance or its insoluble residue should be investigated in the manner described at the end of Chapter IV for substances insoluble in aqua regia, and identified or brought into solution accordingly.

If part of a mixture dissolves in one of the solvents named, it is sometimes rather tempting to filter off the residue and to attempt to make a second solution for analysis from that. This usually results in a duplicate series of operations and consequent waste of time. When the constituents of a 'mixture' have been determined, the extent of its solubility in various solvents may then be used to ascertain how the various radicals are associated with one another. On the other hand, a comparatively soluble mineral, say zinc blende, associated with quartz or some other insoluble material, is obviously best treated in two portions; one which will dissolve in the usual solvents, and one which can be treated as a substance insoluble in acids. It should be noticed in this connexion that the insoluble parts of minerals, particularly silicates, may easily contain such elements as sodium or potassium, and it is therefore advisable to make a complete analysis of the solutions obtained from insoluble residues. Such insoluble silicates are best 'brought into solution' by treatment with sulphuric and hydrofluoric acid, when the sulphates of the cations will be formed without the introduction of alkali. A lead crucible is best for the purpose but details must be looked for in a larger text-book.

In examining the solubility of a substance it is imperative to note if any gases are evolved *and to test for them*, and to observe changes of colour or other physical characteristics accompanying the process of solution. When a suitable solvent has been found, about 50 c.c. of a stock solution should be made for use in identification of cations. A moderately concentrated solution should be made. *Not more than* 10 *c.c. of the stock solution should be taken for the group precipitations.* Larger quantities are to be avoided as they involve

(i) an unnecessarily long time for filtration;
(ii) delay in washing bulky precipitates;

(iii) correspondingly large quantities of reagents to ensure complete precipitation. It should be remembered that the bulk of liquid tends to increase at each operation in geometrical progression.

Before the main analysis is begun the addition of sodium carbonate solution to a small portion of the stock solution will indicate if any cations other than those of the alkali metals, arsenic, and ammonium are present. As a general rule the next step is the precipitation of the first main group of cations which, for reasons explained in Chapter I, p. 16, takes place in two parts. The distribution of the group is shown in **Tables II** and **II A**, pp. 219 and 220.

The First Main Group

(*a*) Group I

If the solution has been made in concentrated hydrochloric acid or in aqua regia it is essential to dilute it, and this in itself may cause a precipitate. This may be a genuine group precipitate (for lead chloride is soluble in concentrated hydrochloric acid) or it may be an oxychloride of bismuth or antimony which should redissolve on addition of a little more acid. If no hydrochloric acid is present in solution a few drops of the dilute acid should be added. If no precipitate forms it is unnecessary to add more acid and the analysis can be continued at Group II below.

If there is a precipitate the acid must be added until there is no change apparent in the amount or condition of the precipitate. As was explained in Chapter I the formation of this precipitate is really incidental to the acidifying of the solution, and it is separated as a measure of convenience. Even so, the chemical significance of the association of these particular elements in the precipitate is quite definite, as **Table I** shows (p. 219).

The normal occurrence here is the precipitation of **silver, mercurous**, and **lead chlorides.**

Abnormal precipitates can be caused by the formation of (1) oxychlorides of bismuth and antimony as indicated above, or possibly, though not a usual thing, from solutions not already containing chloride ion. These will redissolve on addition of more acid; (2) free insoluble acids or their decomposition products; e.g. silicic acid may be set free from a soluble silicate, or sulphur from a thiosulphate or other thio-salt (thiostannates, &c.). These precipitates will not respond to tests for the group cations and if their character is not at once obvious they should be reserved for separate investigation later. Their presence does not vitiate the remainder of the group analysis *provided that positive tests are made for each cation.* In any case conditions which lead to the formation of abnormal precipitates at this stage are rare in elementary work.

The filtration of this group precipitate must be carried out in the cold as lead chloride has a steep solubility curve. It should be washed with cold water after the original liquid has drained off completely. It should not be necessary then to add any of the washings to the filtrate, but there is no harm in adding the first few c.c. The treatment of the precipitate which is discussed on p. 181 (**Precipitate A**) may be left until the group separations have been completed. The further washing of the precipitate can take place while the main analysis is proceeding.

(*b*) Group II

The remainder of the first main group of cations (whose sulphides are insoluble in 0·25 *N* acid) can now be precipitated. Two facts are worth considering here. First, that some of the sulphides, in particular that of arsenic (As_2S_3), do not precipitate well in too low a concentration of hydrogen ion, and secondly, that it is necessary to make the solution 0·25 *N* in acidity eventually in order to precipitate the 'tenderer' sulphides (PbS, CdS, and SnS) completely. If the solution is more dilute than this with respect to hydrogen ions, sulphides of the next group (e.g. zinc sulphide) may begin to come down. One method, therefore, is to precipitate as far as possible in approximately normal acid solution, dilute to 0·25 *N* acid after filtering, and then continue the precipitation; the other method is to add solid ammonium carbonate until a precipitate just begins to form and then to add one-tenth the volume of the solution of bench dilute hydrochloric acid (2 *N*). This gives a solution of approximately the right concentration, and one precipitation should be sufficient for the whole group. Naturally there is no point in doing this if the sodium carbonate test above has caused no precipitate.

Method of precipitation

Owing to the reversibility of the reactions involving sulphide formation from hydrogen sulphide it is desirable to carry out the precipitation in an atmosphere of the gas. This is effected by placing the solution in a *small conical flask* with a cork and a loosely fitting delivery tube. The layer of liquid should be only a few millimetres in depth. If the temperature is raised to 60° before passing in the gas and the flask shaken with a rotary motion during precipitation, the precipitate will coagulate so that it is easy to filter, and will settle readily and allow the end-point of the precipitation to be observed. If no precipitate forms at this stage analysis should be continued at the *Second Main Group*. If a precipitate forms it should be filtered off and the filtrate should be tested by further passage of hydrogen sulphide (after appropriate dilution with a cold solution of the gas if acid more concentrated than 0·25 *N* has been used), and after precipitation appears to have ceased the temperature of the filtrate should be eventually raised to boiling-point for a final test. If this causes a continued production of a yellow sulphide, colloidal in appearance, an arsenate is probably present and is being progressively reduced by the hydrogen sulphide. The reduction can be hastened by using a concentrated acid solution to begin with and then diluting. This method should be adopted if preliminary tests (volatility) suggest the presence of a considerable amount of arsenic. It is important not to boil the solution while the main precipitate is present as the expulsion of the hydrogen sulphide will reverse the precipitation reaction and cause the tender sulphides to redissolve.

The probable order of the solubility products for the sulphides which are precipitated here is **As_2S_3** (least soluble), **HgS, CuS, Sb_2S_3, Bi_2S_3, SnS_2, CdS, PbS, SnS,** but it must be remembered that the total concentration of arsenic even in acid solution is made up mostly of arsenious or arsenic acids. The actual concentration of arsenic cation is always low and precipitation of the sulphide slow in consequence. Otherwise precipitation of the sulphides will follow, for equivalent concentration of their cations, the order of the solubility products. (According to some authors cadmium sulphide is the most soluble.)

Oxidizing agents which have not reacted with hydrochloric acid used in making a solution will almost certainly be reduced by the hydrogen sulphide. Sulphur may be deposited therefore and colour changes occur.

Treatment of the precipitate

The total precipitate from this group may contain any or all of the sulphides enumerated above, and, since oxidation may occur if they are left in the air in a fine state of division (copper sulphide in particular tends to oxidize to copper sulphate), it is best to proceed with their analysis before continuing with the analysis of the filtrate. From the periodic table it can be seen that the elements arsenic, antimony, bismuth, tin, and lead are nearest to the non-metals in position and therefore in character, and will be expected to form anions with greater ease than the remainder. Actually the other elements of the group can form complex anions under certain conditions, but the formation of ions of an 'oxyacid' type is limited to those mentioned (arsenites, stannites, &c.). The actual type of anion used to separate the 'nobler' from the more 'metalloid' elements in the group is the sulphur analogue of the oxyacid, namely, the 'thioacid' anion. These are formed by arsenic, antimony, and tin only. Moreover, just as oxyacid formation is associated always with a high state of oxidation of a metal (cf. CrO_3, Mn_2O_7), in the case of tin a thioacid is formed only by the stannic sulphide and not by the stannous compound. Hence arsenic sulphide (As_2S_3), antimony sulphide (Sb_2S_3), and stannic sulphide (SnS_2) may be regarded as amphoteric sulphides.

To convert an amphoteric oxide into an oxy-anion it is treated with a basic oxide; to convert an amphoteric sulphide into a thio-anion it is treated with a basic sulphide, e.g. sodium sulphide (Na_2S). To convert *stannous* sulphide to the stannic condition first, more sulphur is needed, hence a *basic polysulphide* is required if stannous sulphide is to be converted to a thiostannate. (This is comparable with the use of sodium *peroxide* to convert chromic hydroxide to sodium chromate.) The reagent generally used in the case of the Group II precipitate is ammonium polysulphide, in the form of 'yellow ammonium sulphide'.

It is practically impossible without repeated operations to wash, or even more to dissolve, a precipitate of any size completely while it is still on the filter paper. The precipitate should therefore be transferred to a small basin in the following manner. The filter paper, which should contain the precipitate in a pasty state with no superfluous liquid, should be removed from the funnel, opened up, and laid face downward in a clean dry basin. The back of the paper should be tapped a few times lightly with the fingertips, and on pulling away the paper it will be found that the precipitate is left in the basin. As no liquid has been used to effect the transference, the *minimum* necessary for the subsequent treatment of the precipitate can be used and much time saved in consequence. The basin is half-filled with yellow ammonium sulphide and the mixture warmed for several minutes. If there is an obvious diminution in the quantity of the precipitate after filtration it is advisable to repeat the extraction with a further quantity of solvent. This is one of the places where a large volume of solvent is not a great disadvantage (except that copper sulphide is slightly soluble in this reagent) as it needs further dilution after filtration. The residue, if any, is filtered off and washed with warm dilute ammonium sulphide solution. It can then be left for analysis by the method outlined for copper, cadmium, lead, mercury, and bismuth under **Precipitate B** (p. 184) and the solution left for the subsequent separation of arsenic, antimony, and tin as **Solution B** (p. 182).

The filtrate from the hydrogen sulphide precipitate, or the solution if no precipitate formed, is now analysed for cations of the second and third main groups.

The Second Main Group

(Groups III a and III b: sometimes called Groups III and IV)

This group contains the cations whose sulphides are insoluble in faintly alkaline solution and those whose sulphides are hydrolysed to insoluble hydroxides (see (**Tables II, III,** and **III A**). It is necessary to increase the available concentration of sulphide ion by lowering the concentration of hydrogen ion (see p. 18), which is done by the addition of ammonium hydroxide until the solution is definitely alkaline. As hydroxide precipitation is not part of the main scheme, the concentration of hydroxyl ions is limited as far as possible by first adding about 5 c.c. of 2 *N* ammonium chloride solution, which represses the dissociation of the ammonium hydroxide. (If the original solution was made in concentrated hydrochloric acid there is usually need for very little extra ammonium chloride at this stage.) Even in the presence of ammonium chloride the hydroxides of ferric iron, chromium, and aluminium are precipitated and can be regarded as a separate group. (See p. 175, Alternative Method.) As a little manganese hydroxide and cobalt hydroxide are liable to separate with them and as aluminium and chromium hydroxides are apt to carry down other metals adsorbed upon them, it is advisable to observe their precipitation for the information it gives, but to precipitate the whole group for the purpose of separation. In any case to avoid the premature precipitation of sulphides which will obscure the hydroxide precipitation, the filtrate from Group II must be boiled until quite free from hydrogen sulphide, after which ammonium chloride and ammonium hydroxide should be added.

Unfortunately, a precipitate caused by ammonium hydroxide at this stage may not be proper to the group at all, but may be caused (*a*) by silicic acid, or (*b*) by the re-formation of the salt of a weak soluble acid which has been held in acid solution owing to repression of the dissociation of the acid itself in the presence of hydrogen ion (see pp. 10–11). The salts which generally interfere with the normal course of analysis on this account are the phosphates and oxalates, and less frequently the fluorides of calcium, strontium, barium, and magnesium.

In the event of a precipitate forming on the addition of ammonium hydroxide the anions in question should be tested for as follows:

(*a*) *Silicate*: the precipitation of silica is only likely to occur in a solution made after an alkali or hydrofluoric acid fusion of an insoluble silicate. It is best removed by evaporation of the solution to dryness and redissolving the residue in dilute hydrochloric acid.

(*b*) *Oxalate* and *fluoride*: the treatment of the original solid substance with concentrated sulphuric acid will have revealed the presence of an oxalate or fluoride. The oxalate reaction may be masked by the presence of a carbonate, sulphite, &c., in which case it is better to dissolve a *little* of the precipitate formed at this stage in sulphuric acid and test its reducing power on hot potassium permanganate solution. Oxalates are best removed by evaporation of the solution and ignition, whereby carbonates and oxides of the metals present are formed, but if the procedure suggested on p. 163 is followed, this trouble will be avoided here. By twice evaporating with concentrated hydrochloric acid sufficient fluoride is decomposed to enable the elements of the next group to remain in solution as chlorides and to be detected in their proper places.

(*c*) *Phosphate*: a small quantity of the solution with the precipitate in it is taken and dilute nitric acid added to dissolve the precipitate. *A large excess* of a solution of ammonium molybdate in dilute nitric acid is added, and the appearance of a yellow colour followed by the slow deposition of a heavy yellow precipitate of ammonium phosphomolybdate on warming to 60° shows the presence of the phosphate ion. The following points should be noted.

(i) Make sure that all the molybdic acid has not crystallized out from the molybdate solution before use.

(ii) Remember that twelve molecules of molybdic oxide are required for each atom of phosphorus in order to form the precipitate, and that it will not form in the presence of a large amount of chloride ion or of free phosphoric acid.

(iii) Arsenates, which should no longer be present at this stage of the analysis, give a similar precipitate if the solution is boiled.

Phosphate Separation

If there is no interfering anion present the main analysis can proceed as indicated in the next section. If a phosphate is present the simplest method for removing the phosphate ion relies on the precipitation of ferric phosphate by ferric chloride in acetic acid solution, and the removal of excess iron as basic acetate. As iron is to be added, a small portion of the solution must be used to test for the presence of iron first. It should be boiled with a little dilute nitric acid, and a solution of potassium ferrocyanide added. If iron is present a precipitate of *Prussian blue* will be formed. This may be confirmed by the sensitive thiocyanate reaction (**$Fe^{\cdots}$ 7**).

The precipitate in the main solution is then just dissolved in the minimum of dilute hydrochloric acid, and if iron is present, oxidized with nitric acid as above. The solution is then transferred to a basin and almost neutralized with ammonium hydroxide solution (although not far enough to cause reprecipitation). About 5 c.c. of saturated ammonium acetate solution are then added, the solution warmed a little and ferric chloride added drop by drop until the red colour of ferric acetate develops. (If there appears to be a large excess of iron over phosphate in the original substance, more phosphate must be added as ferric phosphate is appreciably soluble in ferric acetate solution and the phosphate is not then precipitated on boiling.) The precipitate at this stage consists mainly of ferric phosphate. The solution is then boiled vigorously for a few minutes and hydrolysis of the acetate results in the precipitation of the residual iron as basic ferric acetate, or more probably a mixture of the basic acetate and hydroxide. These are filtered off together with the ferric phosphate. The precipitate may also contain any aluminium present and some of the chromium as phosphate and basic acetate, and should be examined for these cations according to the scheme for **Precipitate C** (p. 187). The filtrate must be tested for iron and for phosphate, and if the results are negative, the solution is made alkaline with ammonium hydroxide.

The Group Separation

The main analysis can now proceed as follows. In the event of there being no phosphate or other interfering anion present, or after these have been removed as indicated, the addition of ammonium hydroxide solution should be continued until no further precipitation occurs. The solution, and precipitate if any, should be transferred to the hydrogen sulphide precipitation flask (see Group II) and warmed, after which hydrogen sulphide should be passed in, care being taken to keep air away as much as possible. This prevents the formation of any ammonium polysulphide in which nickel sulphide is soluble. (The use of yellow ammonium sulphide as a group reagent at this point is objectionable on this account, and because of the sulphur which is liable to be set free in the course of the analysis.)

The precipitate formed by the action of hydrogen sulphide will contain the **sulphides** of **manganese, iron, cobalt, nickel,** and **zinc** in addition to the **hydroxides** of **aluminium** and **chromium.** (Note the conversion of both ferrous and ferric hydroxides to the black sulphides.) The sulphides of nickel and cobalt are in their acid-soluble forms and in order to convert them into their insoluble modifications the contents of the flask must be heated to boiling-point for a few minutes while still in an atmosphere of hydrogen sulphide, and shaken to promote coagulation of the precipitate. The precipitate should then be filtered off on a paper moistened with boiling water, and washed with hot ammonium chloride solution to prevent peptization, after which it should be transferred to a porcelain basin and stirred with a solution made by mixing one part of concentrated hydrochloric acid with eight parts of a saturated solution of hydrogen sulphide. It can be examined later according to the scheme given under **Precipitate D** (p. 188).

The filtrate may contain colloidal nickel sulphide and be discoloured in consequence, in which case it should be made just acid with acetic acid, boiled for a few minutes until the sulphide appears to have been deposited, filtered, and then made alkaline again with ammonium hydroxide. It is now ready for analysis for the *third main group*.

The Second Main Group: Alternative Method

Just as the chlorides which are precipitated in making the solution acid are usually removed as a separate group, so the hydroxides which are precipitated on the removal of the hydrogen ion can also be analysed apart from the main group. As the hydroxides of the trivalent cations only fall into this category it is first necessary to oxidize any ferrous ions present to the ferric condition and this is best done by boiling the filtrate from Group II (after it has been freed from hydrogen sulphide) with a little dilute nitric acid or bromine water. Ammonium chloride solution is then added if necessary, followed by ammonium hydroxide until precipitation is complete. The solution is filtered immediately through a paper moistened with boiling ammonium chloride solution and the precipitate washed with a similar solution.

The Group III A precipitate

This precipitate may contain aluminium, chromic, and ferric hydroxides and also a trace of manganese dioxide. Extraction by boiling with strongly alkaline hydrogen peroxide will give a solution of sodium aluminate and sodium chromate which may be filtered off and tested in one portion for aluminium by boiling with ammonium chloride solution (**Al 1**) and in another for chromium by the perchromate test with acidified hydrogen peroxide (**CrO_4''4**). The residual ferric hydroxide may be dissolved in hydrochloric acid and treated with potassium ferrocyanide or potassium thiocyanate (**$Fe^{\cdots}$ 6** and **7**). It is as well to test a portion of this group precipitate for manganese by warming with red lead and nitric acid to form permanganic acid (**Mn 5**).

Group III B

The filtrate from Group III A is treated with a little more ammonium hydroxide solution and the sulphides of manganese, cobalt, nickel, and zinc precipitated in the manner described for the whole group (see above). A separation similar to that described for the whole group precipitate (**Precipitate D**) is followed, except that after digesting the sulphides with cold dilute hydrochloric acid containing hydrogen sulphide the action of alkaline hydrogen peroxide on the filtrate (which must be freed from hydrogen sulphide) will immediately precipitate manganese dioxide, while hydrogen sulphide will precipitate zinc sulphide from the residual solution. Unless the filtrate from the nickel and cobalt sulphides is made very strongly alkaline, the manganese may carry down most of the zinc. Confirmatory tests are suggested in the analysis of **precipitate D.**

The Third Main Group

(Usually called Groups IV and V)

This group contains the cations whose sulphides are hydrolysed to soluble hydroxides or hydrosulphides in weakly alkaline solution. They belong to the first two groups (IA and IIA) of the periodic table (see **Table III**, p. 220), and include the **barium, strontium, calcium, magnesium, potassium,** and **sodium** ions. As the halides, sulphides, and hydroxides of these cations cannot be used for precipitation reactions the separation of members of the group relies mainly on the variation in solubility of their carbonates, sulphates, chromates, and phosphates. In most of the methods devised for the analysis of this group complete separations are almost impossible to achieve, owing to the relatively small differences in solubility for the different cations with the anions used. Hence it is necessary to guard against precipitates due to small quantities of members of the group appearing in the wrong place.

Although the ammonium ion behaves analytically in a manner similar to potassium, the use of ammonium compounds during the course of analysis makes it necessary for the detection of this ion (or of combined ammonia) to be determined in the original compound or mixture at the outset. The presence of a large quantity of ammonium compounds may seriously interfere with the analysis at this stage, calcium carbonate, for instance, being appreciably soluble in a hot concentrated solution of ammonium chloride. It is in fact a very good rule to evaporate the filtrate from the *second main group* to dryness and to drive off the bulk of the ammonium compounds present by ignition.

The carbonate precipitation

Barium, strontium, and calcium are most easily precipitated as carbonates, but the *complete* precipitation of magnesium carbonate is a slow and difficult matter. It is quite easy to prevent its precipitation, however, under conditions which render the other carbonates insoluble, and so the main division of the group lies between barium, strontium, and calcium on the one hand, and magnesium, potassium, and sodium on the other. If the filtrate from the *second main group* (Group III) has been evaporated to dryness and ignited, the residue should be dissolved in the minimum quantity of water, an equal volume of ammonium chloride solution added, and the whole made definitely alkaline with ammonium hydroxide. Ammonium carbonate solution is then added until no further precipitation occurs. If the filtrate from the second main group has merely been concentrated, then it is made alkaline if necessary with ammonium hydroxide solution and ammonium carbonate added directly. The solution is boiled before filtering in order to decompose any bicarbonate (commercial ammonium carbonate is largely a mixture of the bicarbonate and the carbamate) and to granulate the precipitate.

Treatment of the filtrate

After filtering, *one portion* of the filtrate should be tested immediately for magnesium by the addition of sodium hydrogen phosphate solution. A crystalline precipitate, which may separate slowly, indicates the presence of magnesium.

If too much ammonium chloride has been used for the carbonate precipitation some calcium ions will remain in solution and give a precipitate with sodium hydrogen phosphate. If the magnesium precipitate is dissolved in $2N$ sulphuric acid and an equal volume of alcohol added, any calcium present will be precipitated as sulphate and can be filtered off. On making the filtrate alkaline with ammonium hydroxide solution the magnesium ammonium phosphate will be reprecipitated.

The presence of magnesium can be confirmed at any stage of the analysis of this group by adding to the solution containing the suspected magnesium ions a few drops of a solution of *p*-nitrobenzene-azo-resorcinol. On adding sodium hydroxide until the solution is strongly alkaline a blue precipitate will appear if magnesium be present.

The rest of the filtrate can be treated in one of two ways:

(i) The usual method is to evaporate it to dryness and ignite to remove ammonium compounds once more as these interfere with the tests for sodium and potassium. While this solution is evaporating the carbonate precipitate should be analysed for barium, strontium, and calcium as indicated below, after which the tests described for sodium and potassium can be applied to the ignited residue.

(ii) A more expeditious method is to divide the filtrate into two parts. To one is added a small piece of solid sodium hydroxide and after it has dissolved the solution is boiled until it gives no ammonium test with Nessler's solution. Any magnesium carbonate or hydroxide which may have formed is filtered off, the solution neutralized with hydrochloric acid and tested for the presence of potassium by the addition of sodium cobaltinitrite dissolved in acetic acid.

The other portion is similarly treated with *pure* potassium hydroxide, and after filtering off precipitated magnesium compounds, the filtrate is tested for sodium with a solution of potassium pyroantimonate in potassium hydroxide. A blank test should be carried out with the potassium hydroxide used to make sure that it contains no appreciable quantity of sodium.

During the boiling of the solutions to drive off ammonia the carbonate precipitate may be examined for barium, strontium, and calcium.

Separation of barium, strontium, and calcium

This is made to depend on the fact that barium chromate is insoluble in acetic acid, while strontium chromate is soluble in it, calcium chromate being appreciably soluble in water; and secondly, that calcium sulphate is soluble, in the presence of acid, in concentrated ammonium sulphate solution, whereas strontium sulphate is not. The carbonates are therefore dissolved, either on the filter paper or after transference to a basin, in the minimum of dilute acetic acid. As the presence of the chromate ion is undesirable during the separation of strontium from calcium, it is advisable to test a small portion of this solution to see if any barium be present. If it is, then the whole solution is boiled and potassium chromate added until no more yellow barium chromate is precipitated. The presence of barium in this precipitate is confirmed by dissolving it in dilute hydrochloric acid and applying a 'flame test' or by examining it with the aid of a spectroscope. Barium gives a yellowish-green flame and its 'visible' flame spectrum shows several intense green lines, fainter lines in the yellow and orange, and one in the blue. The spectrum should be compared with that given by barium chloride.

If the test for barium shows no positive result it is unnecessary to add potassium chromate to the rest of the solution. This solution, or the filtrate from the barium chromate, as the case may be, is mixed with two-thirds of its volume of concentrated hydrochloric acid. (The resultant solution will be 4 *N* in hydrion. The whole is then treated with its own volume of ammonium sulphate solution (2 *N*) and left to stand for at least ten minutes. Any strontium sulphate formed is filtered off and the presence of strontium confirmed by reducing the precipitate with charcoal (best on a 'charcoal stick') and applying a flame test. The Bunsen flame is coloured carmine by strontium, and the visible flame spectrum contains lines in the red and yellow and a strong one in the blue. The spectrum given by the precipitate should be compared with that given by strontium chloride.

As a check on the ammonium sulphate precipitation a small portion of the filtrate from the barium chromate may be tested with calcium sulphate solution. A slow precipitation should ensue if strontium is present.

The filtrate from the strontium sulphate is made alkaline with ammonium hydroxide solution. The addition of boiling ammonium oxalate solution gives a precipitate of calcium oxalate. This may be dissolved in dilute hydrochloric acid and the flame test applied. The flame is coloured a dull red and the spectrum includes lines in the red, orange, and yellow regions. Comparison should be made with calcium chloride.

Tests for Potassium and Sodium

The filtrate from the carbonate precipitate is evaporated to dryness and ammonium compounds completely removed by ignition. The residue may contain magnesium, potassium, and sodium. It is dissolved in the minimum quantity of water and divided into two portions. To one portion is added a freshly made solution of sodium cobaltinitrite. If potassium is present it will give an intense yellow precipitate of sodium potassium cobaltinitrite $K_2Na[Co(NO_2)_6]$. The presence of magnesium will not interfere with this test. The lilac potassium flame which is red when viewed through cobalt glass (or a solution of copper sulphate) may be used for confirmation.

If magnesium is present (as shown by the sodium phosphate test above) it must be removed from the second portion of the filtrate by the addition of potassium hydroxide. This will precipitate magnesium hydroxide which can be filtered off. A solution is then made by dissolving potassium antimonate in boiling potassium hydroxide solution, and this is filtered into the solution supposed to contain the sodium ions. The mixed solutions are boiled and on scratching the tube with a glass rod the sodium is precipitated as sodium pyroantimonate $Na_2H_2Sb_2O_7$. An intense and persistent yellow flame coloration is characteristic of sodium, but most substances give evidence of traces of this element when viewed spectroscopically.

The earlier group precipitates should now be investigated in order, according to the schemes discussed below. Attention should then be turned to the systematic analysis for acid radicals.

Precipitate A (Group I separation)

This may contain silver, mercurous, or lead chlorides. The separation of these three is effected most simply by a variation in solvent. Lead chloride which is not precipitated completely by dilute hydrochloric acid shows a marked increase in solubility in boiling water; silver chloride is dissolved by the removal of silver ions as complex silver-ammonium ions, i.e. it is soluble in ammonium hydroxide solution, while the low dissociation and 'non-polar' character of mercurous chloride make it difficult to dissolve it without a change of valency, either by the use of an oxidizing solvent or by its own mutual oxidation and reduction.

The precipitate should therefore be transferred to a small basin in the manner described for the Group II precipitate on p. 169. The student should become familiar with the volume relations between the test-tubes, basins, flasks, and beakers that he normally uses, but as a rule it should be sufficient at this point to add to the precipitate one-third of a test-tubeful of water, and to boil the water. The solution is then filtered hot, and lead chloride if present will crystallize as the filtrate cools. Confirm this by the insolubility of the iodide, sulphate, or chromate and the formation of chrome red with alkali (**Pb 2**, **5**, and **6**).

The residue on the filter paper should then be treated in a similar manner with ammonium hydroxide solution. The silver chloride will dissolve (**Ag 1**) and the mercurous chloride will be converted into a mixture of metallic mercury, which in its finely divided condition is black, and mercurammonium chloride (**$Hg_2^{\cdot\cdot}$ 4**). After filtration the solution containing silver can be acidified with dilute nitric acid when the chloride will be reprecipitated. Confirmation of silver is best carried out by reduction of the ammoniacal solution to metallic silver (**Ag 8**).

The black residue is soluble in aqua regia, giving a solution of mercuric chloride in which the presence of mercury can be confirmed by reduction by stannous chloride or precipitation of mercuric iodide (**$Hg^{\cdot\cdot}$ 6** and **1**).

If only a trace of silver is present it may remain as chloride with the mercury residue, in which case it will be left after the treatment with acid and can then be dissolved in ammonium hydroxide and tested as above.

Solution B (Separation of arsenic, antimony, and tin)

The yellow ammonium sulphide solution may now contain ammonium thioarsenate, thioantimonate, and thiostannate (all the sulphides having been oxidized by the polysulphide). On adding dilute hydrochloric acid the free acids will be formed which decompose readily into hydrogen sulphide and the appropriate metallic sulphide, while sulphur will be simultaneously liberated from the polysulphide. By precipitation in a very dilute solution the sulphur will remain in a colloidal condition while the sulphides coagulate; it will not then be retained on the filter paper to confuse the subsequent procedure. The solution should be diluted therefore to several hundred c.c., and made *just* acid to litmus with dilute hydrochloric acid, warmed to boiling-point with shaking and filtered as soon as the sulphides have coagulated. The filtrate can be rejected. The residue will consist of stannic sulphide and the pentasulphides of arsenic and antimony.

The simplest separation of the three sulphides concerned again makes use of their weak acid character, but instead of using a comparatively strong base which will dissolve all of them at once, a variation is made in the alkalinity of the solvents. First the arsenic which is the most acidic of the sulphides is removed by adding to the precipitate in a basin some solid ammonium carbonate and a few drops of water and warming to 40° C. After filtering, the filtrate will give a yellow precipitate of arsenic pentasulphide on acidifying with dilute hydrochloric acid. The presence of arsenic can be confirmed by dissolving part of this precipitate (washed free from hydrochloric acid) in a minimum of concentrated nitric acid, just neutralizing with ammonium carbonate solution and boiling to remove any excess, then testing with silver nitrate for an arsenate (**Arsenates 3**). Alternatively an arsine test may be carried out (**As 7**).

The residue is washed with ammonium chloride solution and again transferred to a basin where it is warmed to 80° C. with 2 or 3 c.c. of milk of lime. The antimony sulphide is converted into calcium thioantimonate which gives a yellow solution, while the stannic sulphide is converted into hydrated stannic oxide. Hence when the precipitate is all colourless the solution is filtered off and acidified with dilute hydrochloric acid when orange antimony pentasulphide (Sb_2S_5) will be precipitated. The presence of antimony in this precipitate may be confirmed by a charcoal test, or by dissolving the antimony sulphide in concentrated hydrochloric acid and pouring into a large quantity of water when the oxychloride (SbOCl) will be precipitated. A white precipitate of sulphur at this stage (derived from the action of the lime on stannic sulphide and acidification of the calcium polysulphide solution so formed) must not be mistaken for antimony sulphide. Any sulphur present can easily be extracted with a little alcohol and carbon disulphide leaving the much deeper coloured sulphide at the interface of the solutions.

The residue from the milk of lime treatment, which will be mostly lime and calcium carbonate, but which may also contain stannic hydroxide, should be dissolved in sufficient warm dilute hydrochloric acid to give a distinctly acid solution. The addition of ammonium chloride and ammonium hydroxide solutions will give a white gelatinous precipitate of stannic hydroxide if tin is present, which may be confirmed by a charcoal test. If more than one element is present in this group the presence of stannous compounds (as well as or as distinct from stannic) can be demonstrated only when the other constituents of the substance are known, and the problem must be left to the ingenuity of the analyst as it is naturally impossible to make any generally applicable rule.

Precipitate B (Separation of Group II A)

The residue after the ammonium sulphide extraction may contain cupric, cadmium, mercuric, bismuth, and lead sulphides. Neither acidity nor alkalinity of solvents can be used with advantage in separating these further, or even to dissolve them, and so recourse is had to *oxidation*. The sulphides are 'boiled' in a basin with about 10 c.c. of moderately concentrated (1:2) nitric acid until no more appears to dissolve. The minute quantity of sulphide ion present is converted into undissociated hydrogen sulphide in the presence of excess hydrogen ion, and is partly removed by boiling and partly oxidized to sulphate ion by the nitric acid. Mercuric sulphide is so insoluble that it is scarcely affected by this treatment. A certain amount of free sulphur will contaminate the residue of mercuric sulphide and even mask its colour to some extent. As the amount of lead present in this group is determined by the solubility of lead chloride in dilute hydrochloric acid, and since lead sulphate is somewhat soluble in nitric acid, the lead will accompany the remainder of the group in the filtrate. The presence of mercury in the residue may be shown by dissolving it in a little aqua regia, boiling off the excess chlorine and diluting somewhat, and then reducing the mercuric chloride formed to insoluble mercurous chloride (white) and finally to mercury (grey) by the addition of stannous chloride ($\mathbf{Hg}^{\cdot\cdot}$ **6**). Potassium iodide will also give a characteristic precipitate ($\mathbf{Hg}^{\cdot\cdot}$ **1**).

The residual lead must now be removed from the filtrate, and this is best effected by evaporation of the filtrate with 5 c.c. of concentrated sulphuric acid until white fumes appear. *After cooling*, the liquid is poured into 10 c.c. of water, the lead sulphate allowed to settle for a few minutes and then filtered. Some basic bismuth sulphate may be formed; but the presence of lead can be confirmed by dissolving the lead sulphate in concentrated ammonium acetate solution and adding potassium chromate. A yellow precipitate of lead chromate insoluble in acetic acid should be formed.

It is now necessary to devise a separation for the copper, cadmium, and bismuth in the filtrate. Again a new principle must be applied and this time the *formation of complex cations* is used. The addition of ammonium hydroxide to the solution of the sulphates precipitates hydroxides (or basic salts) of all these three cations, but those of copper and cadmium redissolve in excess of the reagent to form soluble cuprammonium (or tetrammine-copper) and cadm-ammonium hydroxides. A white residue indicates the presence of bismuth. After filtration this can be dissolved in a very small quantity of concentrated hydrochloric acid and poured into a large quantity of water when bismuth oxychloride will be precipitated by hydrolysis. If this is filtered off and treated with a freshly made solution of sodium stannite (see **Sn'' 2**) a black precipitate of metallic bismuth is formed (**Bi 7**).

The separation of copper and cadmium

Just as complex cation formation was used to separate these elements from bismuth, so *complex anion* formation is used to separate them from each other. This is actually combined with a valency change to a derivative of the *cuprous* ion, which like silver (monovalent) and unlike cadmium (divalent) can form a complex ion with the thiosulphate radical (**Cu 7**). This is decomposed on heating, cuprous sulphide and sulphur being deposited, while the trithionate ion (S_3O_6'') is probably formed in solution. Hence, if the ammoniacal solution from which the bismuth hydroxide, if any, has been filtered is blue, the presence of copper should be confirmed in a portion by acidifying with acetic acid and adding a drop of potassium ferrocyanide solution. A red-brown precipitate of copper ferrocyanide is formed. The rest should be neutralized with dilute sulphuric acid and a few c.c. of extra acid added. (Too much acid will decompose the thiosulphate at once.) A cold concentrated solution of sodium thiosulphate is added until the solution loses its colour momentarily, and the whole boiled for five minutes. The black cuprous sulphide formed is separated by filtration, and yellow cadmium sulphide can be precipitated from the filtrate, after dilution if necessary, by passing in hydrogen sulphide. The presence of cadmium in this precipitate may be confirmed by a charcoal test, or by dissolving it in moderately concentrated hydrochloric acid, boiling off the hydrogen sulphide, adding sodium hydroxide, and heating (**Cd 1**).

A method commonly used for the separation of these cations relies on the differing stabilities of the complex cyanides formed by them in excess of potassium cyanide solution. The equations for the simple ions are:

$$2Cu^{\cdot\cdot} + 10CN' = 2[Cu(CN)_4]''' + (CN)_2$$
$$Cd^{\cdot\cdot} + 4CN' = [Cd(CN)_4]''.$$

Actually in the case of the cuprammonium ion the excess cyanide ion is not discharged as cyanogen but oxidized to cyanate. The reduction to the cuprous state causes such a complete removal of simple cupric ions from the solution that hydrogen sulphide will no longer precipitate cupric sulphide. Hence, after testing a portion of the ammoniacal filtrate for copper with potassium ferrocyanide as above, addition of potassium cyanide to the remainder until it is colourless, followed by the passage of hydrogen sulphide, will cause the precipitation of yellow cadmium sulphide. Cadmium may be confirmed as above.

If the cadmium sulphide precipitate produced by either of these methods is dark coloured owing to traces of lead or mercury which may contaminate it, it may be extracted with moderately concentrated sulphuric acid and reprecipitated after dilution with hydrogen sulphide.

Precipitate C (The phosphate precipitate)

If a phosphate has been found to be present and removed in the manner suggested on p. 172, the ferric phosphate precipitate will carry down with it the aluminium present either as phosphate or basic acetate and some of the chromium as phosphate, as well as traces of the other cations left in solution at this point. It should be tested for the presence of aluminium and chromium and this can be done by applying the relevant part of the group separation described below. It is repeated here for convenience. The amphoteric character of the hydroxides of the cations in question offers a simple means of separation, since extraction with cold sodium hydroxide solution would remove them as sodium aluminate and sodium chromite. This process would be rather slow, and cannot be expedited by heating, as sodium chromite is hydrolysed on boiling with precipitation of a basic chromite (or insoluble chromic hydroxide with adsorbed alkali). By adding hydrogen peroxide, however, the chromite can be converted into the soluble chromate. The phosphate precipitate is therefore transferred to a basin, heated with a solution of sodium hydroxide to which hydrogen peroxide has been added, diluted and filtered. (*See note in* **Precipitate D** *on the use of sodium peroxide.*)

The addition of ammonium chloride (preferably solid) to the boiling filtrate until it is neutral will give a white precipitate of aluminium hydroxide if this element is present, which may be confirmed by the Thénard's blue test on charcoal carried out on the precipitate (p. 136). The presence of a chromate in the filtrate from the aluminium hydroxide may be shown by acidifying with dilute hydrochloric acid and adding more hydrogen peroxide, when the transient blue of perchromic acid will be seen (**CrO_4'' 4**).

Precipitate D (Separation of Group III)

This is the principal precipitate of the second main group and may contain the sulphides of manganese, iron, cobalt, nickel, and zinc and the hydroxides of aluminium and chromium. Nickel and cobalt, which like zinc and cadmium are near the borderline which separates the first two main analytical groups in the periodic table, can form sulphides which in one form are soluble in acid, but in their more stable forms are like the sulphides of the first main group, insoluble in acid of 0·25 *N* concentration. (According to Ostwald's 'law' on the subject the less stable form will be formed first, hence the failure to precipitate in acid solution. It will naturally be the form with the higher solubility, otherwise the unstable form could crystallize from a saturated solution at the expense of the stable form.) Heating the solution and precipitate before filtration (p. 174) and leaving the precipitate in cold dilute acid serve to complete the conversion of these sulphides to their insoluble form. The addition of hydrogen sulphide solution to dilute the acid used prevents the redissolving of any unchanged nickel or cobalt sulphides. The solution must still be definitely acid after the other sulphides have dissolved. (Test a small portion with solid sodium carbonate.) The insoluble nickel and cobalt sulphides are then filtered off and separated as indicated below.

For the remainder of the cations in this group the separation scheme is similar in outline to that used in the first main group. First the amphoteric character of three of the hydroxides and their consequent solubility in caustic alkali effects a separation of aluminium, chromium, and zinc from the rest. In order to avoid the hydrolysis of sodium chromite in hot solutions with consequent deposition of the basic chromite (or insoluble form of the hydroxide as it is sometimes called) an oxidizing agent is added to convert the chromite to the soluble chromate.

The filtrate from the nickel and cobalt sulphides should therefore be boiled free from hydrogen sulphide, and added to a solution of hydrogen peroxide made strongly alkaline with sodium hydroxide solution. The mixture is warmed for a few minutes, preferably in a porcelain basin. *Alkaline hydrogen peroxide is to be preferred to sodium peroxide which needs very careful handling and is liable to ignite paper, wood, or other combustible material in its neighbourhood if it becomes moist.* A precipitate may form consisting of ferric hydroxide (unless this has been removed with the phosphate) and hydrated manganese dioxide (both brown) while the solution may contain sodium aluminate, sodium chromate, and sodium zincate. If the solution is not kept strongly alkaline, then zinc will be carried down with manganese dioxide as zinc manganite (cf. Volhard's determination of manganese. Treadwell and Hall, *Analytical Chemistry*, vol. ii, p. 612, 5th ed., Wiley and Sons Inc. 1919). The precipitate is filtered off and treated as described below (separation of iron and manganese, p. 191).

The separation of aluminium, chromium, and zinc

The filtrate from the iron and manganese hydroxides is boiled in a basin and solid ammonium chloride added gradually until a neutral reaction is obtained. The volume should be kept approximately constant by the addition of water. Since ammonium aluminate is completely hydrolysed to aluminium and ammonium hydroxides, and since the latter is decomposed in alkaline solution, hydrated alumina is precipitated. This precipitate is filtered off and the presence of aluminium in it confirmed by the formation of Thénard's blue (p. 136). The filtrate, which will be yellow if chromate ions are present, is boiled with barium chloride solution and any barium chromate formed is filtered off. The presence of chromium in this may be confirmed by dissolving it in dilute hydrochloric acid and adding hydrogen peroxide when the transient blue of perchromic acid will be seen. An ether extraction will intensify the colour.

The filtrate from the barium chromate after being made alkaline with ammonium hydroxide is saturated with hydrogen sulphide when white zinc sulphide will be precipitated if zinc is present. Confirmation may be made by means of Rinmann's green (p. 136).

By dividing the alkaline filtrate into three portions, adding ammonium chloride to the first and boiling, testing the second with hydrochloric acid and hydrogen peroxide, and saturating the third with hydrogen sulphide, it is possible to save a certain amount of time. The result is not quite so convincing as the method given above and the reduction of the chromate may interfere with the zinc sulphide precipitation.

The separation of iron and manganese

If the filtrate from the phosphate separation was free from iron the precipitate given by alkaline peroxide should consist of hydrated manganese dioxide only, otherwise these two cations are separated by an application of a principle similar to that used in the 'alternative method' given for the third group on p. 175. Ferric hydroxide is insoluble and manganese hydroxide is soluble in ammonium chloride solution. The hydrated oxides are therefore dissolved in the minimum quantity of hydrochloric acid and the chlorine liberated by the manganese dioxide boiled off. An equal quantity of ammonium chloride solution is added and then ammonium hydroxide until the solution is alkaline. A brown precipitate of ferric hydroxide shows the presence of iron which will probably have been established in any case before the test for, or separation of, phosphates was carried out. If not, confirmation can be made by the Prussian blue or thiocyanate tests.

If the filtrate from the ferric hydroxide is saturated with hydrogen sulphide pale pink manganese sulphide is precipitated. Should this precipitate be black it is probably due to the presence of cobalt sulphide, which can be removed by precipitation in acetic acid, after which the manganese can be precipitated in alkaline solution. To confirm the presence of manganese take a *little* of the solution or precipitate and warm with red lead and moderately concentrated nitric acid. Allow the lead peroxide to settle and observe the colour of the permanganate ion in the solution (**Mn 5**).

The separation of nickel and cobalt

The separation of cobalt from nickel presents a parallel to the separation of copper from cadmium in Group II since it combines complex anion formation with a valency change in one of the elements. Although the trivalent cobaltic ion is unstable, it can be stabilized by co-ordination to form complex cations, e.g. $[Co(NH_3)_6]^{\cdot\cdot\cdot}$ or by covalent sharing of electrons to form complex anions, which have so few cobaltous ions in equilibrium with them that they will not respond to the usual tests for cobalt. The complex anions usually made use of are the cobalticyanide and cobaltinitrite ions $[Co(CN)_6]'''$ and $[Co(NO_2)_6]'''$ respectively. If the cobalticyanide ion is used, then the relatively very unstable nickelocyanide ion is decomposed by oxidation with hypobromite and the nickelic oxide filtered off. The presence of cobalt is then confirmed in the filtrate. The nitrite method is described below.

The sulphides of cobalt and nickel are dissolved in the minimum of aqua regia and the solution evaporated to dryness. The chlorides so formed are dissolved in a little water and boiled with sodium carbonate solution. The precipitated carbonates are filtered off and dissolved in a minimum of hot dilute acetic acid. To this solution an excess of a cold saturated solution of sodium nitrite is added and the whole acidified with acetic acid. The mixture is warmed gently with shaking until the evolution of nitric oxide ceases. Sodium cobaltinitrite is thus formed according to the equation

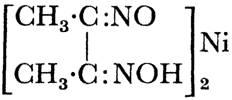
$$Co(NO_2)_2+3NaNO_2+2HNO_2 = Na_3[Co(NO_2)_6]+H_2O+NO.$$

On the addition of potassium nitrate solution the insoluble yellow potassium sodium cobaltinitrite is slowly deposited.

After standing for five minutes it is filtered off and nickel hydroxide may be precipitated from part of the filtrate by the addition of sodium hydroxide solution.

A rather simpler procedure is to add to the chlorides formed as above and dissolved in water a solution of potassium nitrite, the whole being acidified with acetic acid. After standing for ten minutes the filtrate of potassium cobaltinitrite is filtered off and the filtrate tested for nickel.

A borax bead test gives a valuable confirmation for cobalt, and the presence of nickel is shown by treating the remainder of the filtrate with a 1 per cent. solution of dimethylglyoxime in alcohol, making alkaline with ammonium hydroxide and boiling. The red co-ordination complex



$$\left[\begin{array}{l} \mathrm{CH_3\cdot C{:}NO} \\ \qquad\;\; | \\ \mathrm{CH_3\cdot C{:}NOH} \end{array}\right]_2 \mathrm{Ni}$$

is precipitated if nickel is present.

Provided small quantities only are taken the detection of these two cations may be considerably shortened by carrying out the dimethylglyoxime test upon the solution of the chlorides. The cobalt can then be identified by the brownish-red precipitate, insoluble in dilute hydrochloric acid, which it gives when one of its compounds is boiled with a solution of α-nitroso-β-naphthol in glacial acetic acid; or by adding ammonium thiocyanate solution and extracting the bright blue compound formed (probably undissociated ammonium cobaltithiocyanate) with a mixture of amyl alcohol and ether. Dilution with water causes dissociation of the complex and disappearance of the blue colour.

Analysis for Anions

With the exception of the ammonium ion the cations which have been considered have all been simple ions. There are few simple anions, and their detection is relatively easy, but unfortunately most of the common anions are complex and their structure has as much to do with their reactions and the solubilities of their salts as the elements of which they are composed. Hence it is not so easy to correlate their behaviour with the periodic law as in the case of cations, although ultimately this can be done. (Since the elements of the A and B subgroups of the periodic table resemble each other most in their highest states of oxidation, which are also the acid-forming states (if any) of the elements, the short form of Mendeleef's Table shows the similarity in anions better than the extended form.) It also follows that it is not so easy to systematize the tests for their detection, but it must be remembered that the analysis of a substance is a single process and that a great deal of the information obtained in the preliminary examination and in testing for cations is patently or implicitly giving evidence for the presence or absence of many of the anions.

It is as well, therefore, at this stage to recapitulate what has been observed so far and to see how far it can assist in determining the anions present.

1. Colour

Colour in the solid state is not a reliable guide. Colour in solution is usually associated with the cations of the 'transition' metals (Cr, Mn, Fe, Co, Ni, Cu), but chromates, dichromates, and permanganates are yellow, orange, and purple respectively, while co-ordinated metal anions of this series, e.g. ferrocyanides, usually form coloured salts.

2. The effect of heat on the substance *(with regard to anions)*

Substances, either natural or artificial, which have been subjected to a high temperature at any time are not likely to contain any but the thermally most stable anions. The following classification covers the effect of heat in most cases.

(*a*) Simple ions (halides, oxides, sulphides) will as a rule be unaffected, although sulphides may be oxidized to sulphur dioxide in air.

(*b*) *Apart from most of the normal alkali salts* which are quite stable, salts of oxyacids tend to decompose in such a way as to leave a simple ion, and usually leave the metal combined with the most electronegative element in the anion. This gives two main classes of decomposition.

(i) *Oxygen* is given off and a halide, oxide, or stable alkali salt is left (Exx. halogen oxyacids, peroxides, 'per-salts' such as persulphates; also chromates, dichromates, and permanganates).

(ii) *A volatile acidic oxide* (which may be dissociated into a lower oxide and oxygen) is given off and an oxide left (Exx. sulphites, sulphates, nitrites, nitrates, arsenites, arsenates, and carbonates).

Where the acid oxide is not volatile nothing will be given off except, perhaps, steam (Exx. phosphates, silicates, borates). Note the gradual change in the character of the decomposition as the periodic groups with which the anions are associated change.

(*c*) As oxygen is associated with the decomposition of oxyacids, so *sulphur* may accompany the decomposition of thioacids (e.g. thiosulphates) or *chlorine* that of chloroacids (e.g. complex chlorides such as the platinichlorides).

(*d*) *Nitrogen* comes from ammonium nitrite or dichromate, and *nitrous oxide* from ammonium nitrate, by autoxidation of the ammonium radical.

(*e*) *Hydrides of the non-metals* may be given off if water or acid salts are present (e.g. HCl from $AlCl_3.6H_2O$; H_2S from CaS in the presence of water; PH_3 from Na_2HPO_3 or NaH_2PO_2).

(*f*) Salts of organic acids may give, with or without charring, hydrogen, carbon monoxide, carbon dioxide, or inflammable vapours (formates, acetates, oxalates, tartrates).

(*g*) Salts of cyanogen acids may give nitrogen or cyanogen (see p. 64).

(*h*) Water vapour may come from water of crystallization or from the decomposition of acid salts (bicarbonates, secondary phosphates, &c.).

If the substance has been heated *with charcoal* deflagration will be noticed with those substances most ready to give off oxygen; e.g. nitrates, chlorates, perchlorates, peroxides, persulphates, permanganates.

Interaction of constituents on heating

This is a most important consideration in the analysis for anions and cannot be 'generalized'. The most common effect is mutual oxidation and reduction. Halogens may be evolved on oxidation of halides, sulphur dioxide on oxidation of sulphides or reduction of sulphuric acid (e.g. in acid sulphates). Oxides may be evolved from the oxidation of elements present (e.g. carbon, sulphur).

3. The effect of solvents

It is impossible to summarize here all the information on solubility of salts given in detail in Chapters II and III, but if the cations in a mixture of substances are known the behaviour of that mixture towards solvents, and towards water in particular, will give a certain amount of eliminating evidence. It will have been observed that as a general rule the number of soluble salts formed by cations increases as one proceeds from the first to the last analytical group. The common salts of the alkali metals are all soluble in water whereas very few salts of silver or lead are soluble. The analytical chemistry of each of the cation groups should recall the solubility characteristics of the salts concerned. The following lists may be useful for reference, but the term *soluble* is both relative and elastic, and it is impossible to cover all such cases as the formation of soluble acid salts (e.g. bicarbonates), insoluble basic salts (e.g. $BiO(NO_3)$), or soluble complex salts (e.g. double oxalates or tartrates). *Only the cations which have been considered in this book have been included.*

(*a*) **Water**

(i) All known hypochlorites, chlorates, perchlorates, thiosulphates, persulphates, nitrites, nitrates, formates, and permanganates are appreciably soluble in water (silver and barium thiosulphates, silver and lead formates, and silver nitrite are very sparingly soluble; potassium perchlorate is almost insoluble).

(ii) Practically all alkali (Na, K, NH_4) salts are soluble. (For exceptions see pp. 127–8.) The *alkali salts only* of the following are soluble: iodates, sulphites, phosphates, arsenates, arsenites, carbonates, oxalates, and tartrates. (Note alkaline earth and magnesium bicarbonates, bisulphites, acid phosphates.)

(iii) The *alkali* and *alkaline earth* (including *magnesium*) *salts only* of the following are soluble in or hydrolysed by water: bromates (except barium), oxides and hydroxides (not magnesium), peroxides, sulphides, cyanides, ferrocyanides, ferricyanides (mercury cyanide is also soluble in water).

(iv) Most chlorides, bromides, iodides, sulphates, acetates, cyanates, and thiocyanates are soluble.

Principal exceptions: the *chlorides* and *bromides* of the silver, mercurous, and cuprous ions, the *iodides* of copper, silver, mercury, lead, and bismuth, and basic chlorides of bismuth, antimony, and magnesium ('Sorel cements'); lead chloride and bromide are sparingly soluble. Also barium, strontium, and lead *sulphates*; silver and lead *cyanates*; silver, mercury, lead, and cuprous *thiocyanates*; silver, mercury and certain basic *acetates*. (For details see appropriate anions in Chapter II.)

(v) The only soluble *fluorides* are those of the alkali metals, silver, and mercury.

The soluble *chromates* are those of the alkali metals, magnesium, calcium, and strontium. The solubility relationships of the other chromates are complicated by hydrolysis to basic chromates and other reactions which are briefly discussed on pp. 103 and 120.

Interaction in solution is just as likely to give evidence of the general character of the constituents as interaction on heating, but such interaction is more likely to occur in artificially mixed substances than in those occurring naturally together. The liberation of halogens (especially iodine) by oxidizing reagents and the decomposition of salts of weak and volatile acids (H_2CO_3, H_2SO_3) by acid salts, or the reduction of strong oxidizing agents by the action of sulphides, sulphites, nitrites, and the lower oxy-acids generally, or by any metal of variable valency in a low valency state, should be watched for. There may also be evidence of interaction with the water itself such as the evolution of oxygen from peroxides; of hydrogen sulphide, ammonia, phosphine, methane, or acetylene (i.e. volatile hydrides) from binary compounds of the appropriate non-metals (sulphides, nitrides, &c.)

(*b*) Dilute hydrochloric acid

With the exception of the insoluble substances described on p. 157, and a few of the more insoluble sulphides which require aqua regia for their solution, all those compounds which are insoluble in water will dissolve in hydrochloric acid of adequate strength or in dilute nitric acid. The action of dilute hydrochloric acid on the dry substance is also of great importance in determining the anions present, since any unstable acid giving rise to volatile products will be set free and decomposed by it, while weak volatile acids will be liberated by warming the solution. It is important that tests should be made for all gases that might be evolved. These are:

CHLORINE from hypochlorites. If the hydrochloric acid is at all concentrated, chlorine will be set free by strong oxidizing agents such as permanganates. Chlorates will liberate a mixture of chlorine and chlorine peroxide on warming. Bromates may give both chlorine and bromine.

OXYGEN. This will come, especially on warming, from true peroxides and per-salts (i.e. derivatives of hydrogen peroxide). In the case of persulphates it will be ozonized.

HYDROGEN SULPHIDE from soluble sulphides. This is the reverse of the sulphide precipitation, the concentration of the acid determining the liberation of hydrogen sulphide. Many naturally occurring sulphides are in peculiarly insoluble forms. The simultaneous precipitation of sulphur shows the presence of a polysulphide.

SULPHUR DIOXIDE from all sulphites (better on warming). The simultaneous precipitation of sulphur shows the presence of a thiosulphate, or interaction of hydrogen sulphide with the sulphur dioxide.

OXIDES OF NITROGEN fron nitrites.

CARBON DIOXIDE from carbonates and cyanates (since cyanic acid is hydrolysed to carbonic acid).

HYDROCYANIC ACID from cyanides (other than the unionized mercuric cyanide) and from complex cyanides on boiling.

Acetic acid vapour will be set free from acetates on boiling with dilute acid. *Bromine* and *iodine* are liberated from bromides and iodides in the presence of oxidizing agents.

4. The effect of concentrated sulphuric acid

If it has not been done already the effect of hot concentrated sulphuric acid on the dry substance should be ascertained. In this case any acid more volatile than sulphuric acid will be liberated and any acid which reacts with sulphuric acid to give volatile products can also be detected. Naturally the reactions observed with dilute hydrochloric acid will recur on heating the solid with concentrated sulphuric acid and may obscure this second test. Apart from such repetitions the products of reactions may be:

From the HALOGEN ACIDS: *hydrogen fluoride* from fluorides; *hydrogen chloride* from chlorides; *hydrogen bromide* and *bromine* (which will first colour the solution and then be evolved) from bromides; *hydrogen iodide* and considerable *iodine* from iodides.

Chlorine peroxide (explosive) from chlorates; bromine from bromates. Chlorine is given off from chlorides in the presence of oxidizing agents.

From NITRATES: *nitric acid vapour* and *nitrogen peroxide* on heating.

From CARBON ACIDS: *carbon monoxide* from formates and the cyanogen acids except thiocyanates (which give a foul smell of carbonyl sulphide COS) and cyanates (CO_2). Hydrocyanic acid is hydrolysed to formic acid; hence the similarity in reaction.

Carbon monoxide and *carbon dioxide* from oxalates and tartrates (the latter will 'char' with formation of free carbon); *acetic acid vapour* from acetates (converted to ethyl acetate in the presence of alcohol).

From METAL ACIDS: red crystals of *chromic anhydride* (CrO_3) are formed from a chromate; *chromyl chloride* CrO_2Cl_2 (like bromine in appearance) from chromates in the presence of chlorides; violet *manganese heptoxide* vapour (explosive) is set free from permanganates.

Sulphur dioxide may be liberated by any reducing agent, anion or cation (e.g. metals, insoluble sulphides, carbon and organic matter, hypophosphites, &c.).

5. It will be seen that the only anions which do not show some sort of reaction with either dilute hydrochloric acid or concentrated sulphuric acid are: perchlorates and iodates; oxides and hydroxides; sulphates; phosphates, arsenites, and arsenates; silicates, borates, and possibly chromates. Most of these will have been discovered in the course of the cation analysis (see **6** below). Apart from perchlorates and oxides these radicals are all fairly easy to identify by specific tests which are described below in their appropriate places.

6. Evidence from the analysis for cations

The identification of arsenic, chromium, manganese, or iron may have been due to the presence of arsenites, arsenates, chromates, permanganates, ferrocyanides or ferricyanides respectively, and it should be remembered that many of the metals are capable of forming complex anions not usually considered in schemes of analysis. In addition to the metal anions the phosphate, oxalate, and silicate radicals are often discovered in the normal course of the analysis for cations.

Identification of anions in solution

The information about anions present in a substance which will have been accumulated at this point will not be conclusive except in a few cases, notably the reactions with dilute hydrochloric acid. Something more systematic is usually necessary in order to complete the analysis, and here, as with cations, reactions in solution are found to be the most satisfactory. The ideal reagent would be a soluble weak base, forming salts with a large range of solubility, the concentration of whose cation can be regulated by varying the concentration of hydroxyl ion in the solution (cf. H_2S in cation analysis). Unfortunately none of the common bases fulfil these conditions. It is possible to compare the sulphides of the cations with, say, the silver salts of the anions, since these can be arranged in three main divisions: those soluble in water, those soluble in dilute acids, and those insoluble in dilute acids, while the concentration of silver ion can be controlled to some extent by the formation of complexes; but it is a false analogy. The varying solubility of series of salts are in fact used more to show the presence or absence of certain groups of anions after which individual confirmatory tests, often in solutions containing several anions, are relied upon. The actual separation of anions from one another is usually possible but in most cases it is unnecessary. An attempt has been made below to indicate any properties which are common to the members of these anion groups, and which cause them to be associated.

From the study of the cation groups it will be remembered that in general the number of insoluble salts formed decreased from the first to the third main group, and therefore it is not surprising to find that the use of one cation from each group (namely barium, nickel, and silver) is sufficient for a preliminary classification of the anions. From a review of the solubilities of salts in water it is seen (*a*) that the alkali salts are practically all soluble in water, (*b*) that the majority of heavy metal salts are insoluble. The greatest variety of solubility is found in the salts of the alkaline earth cations, and a division can be made between anions whose barium salts are soluble or hydrolysed by water, and those which can be precipitated from aqueous solution. The groups so formed are:

Soluble barium salts.

Salts of all halogen acids except the fluoride, bromate, and iodate; the oxide, hydroxide, sulphide (hydrolysed), and persulphate; the nitrite, nitrate, and hypophosphite; salts of the cyanogen acids, formate and acetate (i.e. the monobasic carbon acids), and the permanganate.

Insoluble barium salts.

The fluoride, bromate, and iodate; the sulphite, thiosulphate, and sulphate; salts of all phosphorus and arsenic acids (except hypophosphite); the carbonate, oxalate, and tartrate (dibasic carbon acids); the silicate, fluosilicate, borate, and chromate.

The distribution of these anions in the Periodic Table is given in **Table IV**, p. 221.

Anions forming soluble barium salts

It should be noticed that the anions which form soluble barium salts are mostly those of strong acids of the monobasic type, and associated with the most electronegative elements (except fluorine). The weakness of hydrofluoric acid and its probable dibasicity (H_2F_2) and the similarity in behaviour of the cyanide ion to a halide ion are points of interest here. This group of anions can be subdivided further according to the behaviour of their silver and nickel salts.

The following silver salts are insoluble in water and in cold dilute nitric acid: chloride, bromide, iodide, sulphide, cyanide, thiocyanate, ferrocyanide, and ferricyanide. Silver hypochlorite decomposes into silver chloride, which is precipitated, and silver chlorate. Silver sulphide is dissolved slowly by *hot* dilute nitric acid. Note again the association of the cyanogen and halogen groups.

Of these anions, the *nickel* salts of the following are insoluble in water: sulphide, cyanide, ferrocyanide, and ferricyanide.

The following silver salts are sparingly soluble in water and readily soluble in dilute nitric acid: nitrite, cyanate, formate, and acetate. Silver persulphate is unstable and forms black silver peroxide on decomposition; hydrogen peroxide in slightly alkaline solution has a similar effect. Hypophosphites give with silver nitrate a precipitate of white silver phosphite and metallic silver, the phosphite changing eventually to yellow silver phosphate and more silver.

The *nickel* salts of all these anions are soluble in water.

The remaining silver salts in this group are quite soluble in water, namely the chlorate, perchlorate, nitrate, and permanganate (all strong oxidizing agents). Their *nickel* salts are also soluble.

Anions forming insoluble barium salts

Of the insoluble barium salts the sulphate and fluosilicate are insoluble in any dilute acid, hot or cold, and in concentrated hydrochloric or nitric acids, while the fluoride, bromate, and iodate are soluble with difficulty in acids. The remainder are all soluble in or decomposed by dilute nitric acid and the same is true of the corresponding silver salts. Apart from the colour of some of them (orthophosphate and arsenite *yellow*, arsenate *brown*, and chromate *terra-cotta*) the character of these silver salts is not therefore of great help here.

The varying solubility in acids of the *calcium* salts of this group can be used for further classification. They are all insoluble in water except the bromate, sulphate, thiosulphate, and chromate, but the following are *soluble in dilute acetic acid*: sulphite, phosphite, ortho-, meta-, and pyrophosphate, arsenite and arsenate, carbonate, tartrate, silicate, borate.

The remaining calcium salts in this group are insoluble in acetic acid. These are the fluoride, fluosilicate, iodate, and oxalate.

The application of this grouping is explained in detail below.

Method of analysis for anions in solution

In order to carry out reactions for anions in solution it is necessary to remove those cations which would interfere by forming insoluble compounds with the anions in question. The anions are therefore converted to their sodium salts by boiling the substance with a concentrated solution of sodium carbonate. All cations other than those of the alkali metals will be converted to their carbonates, hydroxides, or oxides, and the sodium salts of the anions will be left in solution. Arsenic may be converted from the cationic to the anionic condition. If the substance contains only alkali metals (which will have been found from the cation analysis) the aqueous solution must be tested for acidity or alkalinity. If neutral or alkaline there is naturally no need to add sodium carbonate. (A very insoluble substance which dry tests show to be of a salt-like character (see p. 160) should be fused if possible with a mixture of sodium and potassium carbonates and the melt extracted with sodium carbonate solution.) The aqueous extract must now be neutralized with acid, and it is important that the radicals of any acids used for neutralization should be tested for independently. *A portion should be reserved for this purpose.* The main bulk of the solution can then be conveniently neutralized by adding, drop by drop, just the right amount of dilute nitric acid.

It is probably best at this stage to boil off the carbon dioxide liberated from the excess sodium carbonate, otherwise a calcium precipitate will always appear subsequently and a large number of unnecessary tests may be made in consequence. On the other hand, it must be remembered that all the anions normally detected by the action of dilute acid, and a few others, will be partly or wholly removed at the same time. That is to say, this method of approach must preclude the finding in solution of *carbonate* (added and decomposed), *oxides* and *hydroxides* (which have been left behind or neutralized), while *hypochlorites*, derivatives of hydrogen peroxide (*peroxides* and *persulphates*), soluble *sulphides*, *sulphites*, *thiosulphates*, *nitrites*, *cyanides*, and *cyanates* are all liable to be decomposed along with the excess sodium carbonate. A fine deposit of sulphur would indicate the presence of a thiosulphate here. To cover the comparatively few cases where sodium carbonate is not necessary these anions have been included in the scheme outlined below. *Fusion* with sodium carbonate will destroy those radicals unstable to heat such as nitrates, chlorates, &c., and therefore should be applied only to insoluble residues. In practice it will be found that the use of the relevant information given for each anion will simplify and very considerably shorten the procedure in solution. It should be kept in mind that a great deal of the knowledge derived from preliminary consideration is of an *eliminating* character.

The test for nitrate

If the main solution for anion analysis is to be made neutral by adding dilute nitric acid, a small portion of the solution should be tested for nitrate ions first. This can be done by means of the brown ring test (**Nitrates 4**) which is satisfactory if nitrites and bromides in particular, and a few other radicals which may interfere by giving coloured reaction products with concentrated sulphuric acid, are absent. To make a more conclusive test decompose any nitrite present by boiling the test portion of the solution with urea and dilute sulphuric acid; then boil it with a little concentrated caustic soda to destroy any ammonium compound which may be there (these should not be there if the substance was boiled with sodium carbonate solution) and finally add Devarda's alloy (or aluminium or zinc dust if the alloy is not available) heat, and test with Nessler's solution for the presence of ammonia.

Separation of the anions into groups

A. Separation of the insoluble calcium salts

Of the anions forming insoluble barium salts the majority also form insoluble calcium salts, and these anions can be removed from a portion of the solution for anion analysis by making it *just* alkaline with ammonium hydroxide and then adding calcium nitrate solution until there is no further precipitation. The advantage of using calcium nitrate solution (and later on barium nitrate solution) instead of the more usual chloride reagents is that the filtrates can be directly tested with silver nitrate. Before filtering off the calcium precipitate it should be allowed to stand and the vessel (a small flask is best) scratched with a glass rod to ensure complete precipitation, calcium iodate in particular being slow to form. The precipitate will contain the calcium salts of the following anions: fluoride, iodate; (sulphite); salts of all the phosphorus and arsenic acids *except hypophosphite*; (carbonate) oxalate, tartrate; silicate, fluosilicate, borate. Sulphite and carbonate will in almost all cases have been removed at this stage. The precipitated salts are all white, and can be differentiated as outlined under **Group A** below.

B. The barium nitrate precipitation

After the removal of the insoluble calcium salts, the remaining insoluble barium salts can be precipitated by the addition of barium nitrate solution. Precipitation should be carried out with a hot solution to cause the barium chromate and sulphate formed to 'granulate', then the solution should be allowed to cool and the vessel scratched to ensure the precipitation of the sparingly soluble barium bromate and thiosulphate (this anion may have been destroyed by the nitric acid treatment of the solution). The identification of these four ions is discussed below under **Group B**. After allowing the precipitate to stand for some minutes it should be filtered off. If chromate is present it will be yellow, otherwise it will be white.

C. The nickel nitrate precipitation

If the excess of ammonium hydroxide has not already been removed, the filtrate from the barium precipitate should be boiled until it is neutral. It will then contain any anions whose barium salts are soluble or hydrolysed in water, and if calcium and barium nitrates have been used as precipitants it can be used, by means of nickel and silver nitrates, for a further separation into groups of those anions listed above which give soluble barium salts. Free oxide, hydroxide, or peroxide will all have been neutralized by treatment with nitric acid. The anions concerned therefore are all the monobasic anions except fluoride, bromate, iodate, and metaphosphate, and in addition, the sulphide, persulphate, ferrocyanide, and ferricyanide.

From a neutral solution containing these anions, nickel nitrate solution will give precipitates with the sulphide (black), cyanide (pale green), ferrocyanide (pale bluish-green), and ferricyanide (brown). If a precipitate occurs with nickel nitrate independent tests should be made for these anions in the original anion solution as indicated in **Group C** below. The colour of the precipitate, which should be filtered off, may give some indication.

D. The silver nitrate precipitation

The filtrate should be concentrated if necessary at this point and silver nitrate solution added. This will give a precipitate with all the remaining anions except chlorate, perchlorate, nitrate, and permanganate, although dilute solutions of formate, acetate, and even nitrite may not give appreciable precipitates. In most cases the precipitate will be white, but silver iodide is yellow, while hypophosphites (and formates on warming) will cause a black deposit of metallic silver by reduction and any persulphate left in the solution may give a black precipitate of silver peroxide. The precipitate should be filtered off and appropriate tests made for the anions of **Group D** which may be subdivided as shown below into: (*a*) those whose silver salts are insoluble in dilute nitric acid: chloride, bromide, iodide, and thiocyanate (hypochlorite being included in this group also); and (*b*) those which give a precipitate with silver nitrate which is soluble in dilute nitric acid; namely, persulphate, nitrite, hypophosphite, formate, acetate, and cyanate.

E. The soluble silver salts

The filtrate from the silver precipitate can be used directly to test for the anions of **Group E** enumerated above. Although these have been described at the end of the detailed tests it is usually more convenient to start with this solution while the other precipitates are being washed.

Group A: the precipitated calcium salts

After this precipitate has been filtered off it should be shaken vigorously with dilute acetic acid. If there is any residue it should consist of calcium fluoride, fluosilicate, iodate, or oxalate, and these anions should be tested for as follows:

FLUORIDE. A portion of the residue or of the original substance is mixed with finely divided silica and treated with a drop of concentrated sulphuric acid in an iron crucible. The silicon fluoride formed is detected by hydrolysis in a drop of water on a watch-glass (**Halides 5**). *Relevant information*: action of H_2SO_4 on dry substance.

FLUOSILICATE. The same test applied to the original substance without admixture of either sodium fluoride or silica will show the presence of a fluosilicate.

IODATE. A portion of the residue is dissolved in dilute hydrochloric acid and a little sulphur dioxide passed in or sodium bisulphite added. Iodine is immediately liberated, which can be detected with starch solution. *Relevant information*: effect of heat.

OXALATE. The remainder of the residue is dissolved in dilute sulphuric acid and treated with a drop of dilute potassium permanganate solution and warmed. Decolorization of this solution shows the presence of an oxalate. *Relevant information*: effect of heat and of concentrated H_2SO_4.

A high concentration of sulphate ion in the original anion solution may cause a precipitate of calcium sulphate which will not respond to these tests.

If there is no residue after shaking with acetic acid, then these anions are absent, and tests can be confined to the following which must be carried out in all cases where a calcium precipitate occurred.

SULPHITE and CARBONATE. These will have been identified by the action of dilute hydrochloric acid. If sulphur dioxide is given off the gases should be passed through potassium dichromate solution acidified with sulphuric acid, and then through lime water, otherwise it is difficult to obtain a satisfactory test for carbon dioxide.

PHOSPHITE. Except for the formation of insoluble calcium and barium salts the behaviour of a phosphite is very similar to that of a hypophosphite. In the absence of the latter the formation of phosphine on heating the dry substance is probably the best confirmation of its presence. Otherwise a portion of the acetic acid solution of the calcium salts should be treated with zinc and sulphuric acid to give phosphine, but this is not a very satisfactory procedure.

PHOSPHATES. A portion of the acetic acid solution of the calcium salts is treated with a large excess of ammonium molybdate, and warmed *not above* 60°. A yellow precipitate of ammonium phosphomolybdate indicates the presence of a phosphate.

The coagulation of albumen solution by free metaphosphoric acid distinguishes this anion from that of pyrophosphoric acid. Metaphosphates and pyrophosphates are converted to orthophosphates on boiling.

The presence of phosphate is often detected during the cation analysis.

The presence of ARSENITE and ARSENATE will have been revealed by cation analysis, a slow progressive precipitation in Group II of the cations being associated with the presence of arsenate. In the absence of phosphate the ammonium molybdate test for arsenic can be carried out in nitric acid solution (**Arsenates 4**). The formation of Scheele's green can be used with the anion solution for arsenite (**Arsenites 4**).

TARTRATE. The remainder of the acetic acid solution will give a silver mirror when added to ammoniacal silver nitrate solution and warmed. (If phosphites are present they may interfere with this test.) *Relevant information*: effect of heat and of concentrated H_2SO_4 (especially *charring*).

SILICATE. The original substance is mixed with a little sodium fluoride in an iron or nickel crucible. A drop of concentrated sulphuric acid is placed on the mixture and a moist watch-glass placed over the crucible for a few seconds. A 'skin' of silica on the moisture on the convex surface of the watch-glass indicates the presence of silica or a silicate (**Silicates 2**).

BORATE. The original substance is treated in a small basin or crucible with sulphuric acid and alcohol, and warmed. The alcohol vapour is ignited and burns with a green flame if borates are present. The turmeric test can also be applied to the anion solution (**Borates 2** and **5**).

Group B: the precipitated barium salts

If the precipitate given by barium nitrate is not completely soluble in dilute nitric acid, the residue should be barium sulphate or else sulphur from the decomposition of the thiosulphate, which can be extracted with alcohol and carbon disulphide. In any case the thiosulphate will in most cases have been destroyed at this stage. If the acid solution is orange a chromate is probably present. The other anion in this group is the bromate ion. Barium bromate, though reasonably insoluble, forms very slowly and dissolves in acids with difficulty. The following confirmation should be attempted for these anions.

BROMATE. The nitric acid solution of the barium precipitate can be reduced with zinc, and the solution then tested for a bromide with chlorine water and carbon disulphide. *Relevant information*: effect of heat and of acids.

SULPHATE. Reduction of the barium sulphate residue on a charcoal stick and subsequent evolution of hydrogen sulphide on treatment with acids is the best confirmation. In the absence of other sulphur anions this can be done with the original substance. If a portion of the original anion solution is acidified with dilute nitric acid and strontium nitrate is added, there should be a slow-forming precipitate of strontium sulphate.

THIOSULPHATE. By themselves thiosulphates are easily identified by the effect of dilute acids on the dry substance or its solution, but in the presence of sulphite and sulphide the evidence is confusing. It is possible to remove the sulphide by shaking a neutral solution containing these anions with cadmium carbonate, after which the sulphite can be removed by the addition of strontium nitrate, and the filtrate tested for thiosulphate by the addition of hydrochloric acid. *Relevant information*: effect of heat.

CHROMATE. Reduction of the *cation* solution by hydrogen sulphide with appropriate colour changes, and subsequent detection of chromium, may have shown the presence of a chromate. A portion of the anion solution acidified with hydrochloric acid can be treated with hydrogen peroxide in the presence of ether, when the blue perchromic acid will be formed. *Relevant information*: colour; deflagration on charcoal.

Group C: the precipitated nickel salts

These are the sulphide, cyanide, ferrocyanide, and ferricyanide.

SULPHIDE. The nickel precipitate will be black or very dark brown. The original anion solution will give a purple coloration with alkaline sodium nitroprusside solution, and a black precipitate with sodium plumbite. For insoluble sulphides carry out the test with tin and hydrochloric acid (**Sulphides 9** and **3**). *Relevant information*: effect of dilute HCl; reduction of concentrated H_2SO_4; effect of heating in air.

CYANIDE. Nickel cyanide is pale green. The original substance is warmed with concentrated hydrochloric acid and any acid vapour escaping absorbed on a filter paper moistened with sodium hydroxide solution. This is then treated with ferrous sulphate (to form ferrocyanide) and ferric chloride solutions and then hydrochloric acid, when a Prussian blue stain will form if cyanide was present.

FERROCYANIDE. Nickel ferrocyanide is bluish green. Test the original anion solution with ferric chloride solution. A Prussian blue precipitate is formed by ferrocyanides. If the precipitate is obscured by the presence of a thiocyanate (q.v.) dilute considerably, filter, and wash the precipitate with ether. The blue residue, if any, will then be seen clearly.

FERRICYANIDE. Nickel ferricyanide is brown. A Prussian blue precipitate ('Turnbull's blue') will be given by the original solution on the addition of ferrous sulphate.

Relevant information for cyanides (simple and complex): concentrated H_2SO_4 gives carbon monoxide; also effect of dilute HCl on soluble cyanides.

Group D: the precipitated silver salts

Comments on the character and colour of the silver precipitate have already been made. The precipitate should be transferred to a basin and warmed with dilute nitric acid. If it is black, due to the presence of metallic silver, it may give a rather discoloured residue. If there is a residue at all the following anions may be present, and should be confirmed: chloride, bromide, iodide, (hypochlorite), thiocyanate.

HYPOCHLORITE will have been detected by the action of dilute hydrochloric acid on the original substance. It will appear in the silver precipitate as silver chloride.

THIOCYANATE. Vigorous heating with nitric acid will have converted silver thiocyanate to silver sulphate which is soluble and carbon dioxide, but as a rule it will remain as a residue. It is detected in the anion solution by the addition of ferric chloride which gives an intense red coloration due to ferric thiocyanate which can be extracted with ether. *Relevant information*: effect of heat and of concentrated H_2SO_4.

BROMIDE and IODIDE. Suspend some of the silver precipitate in sulphuric acid, add granulated zinc, and warm till the reaction is vigorous. Decant the clear solution after a minute or two, add carbon disulphide to a portion, and test with chlorine water (**Halides 8**). In the absence of cyanide the anion solution can be used directly for this test.

CHLORIDE. If the other anions of this group are absent, the remainder of the solution obtained by the zinc reaction should give a white precipitate of silver chloride on the addition of silver nitrate. If the other anions are present the original substance, or better the residue from evaporating part of the anion solution, should be mixed with potassium dichromate and sulphuric acid, heated, and the distillate hydrolysed with alkali and tested for chromate by the perchromate test (**Halides 4; Chromates 4**). (Fluorides give chromyl fluoride similar to chromyl chloride.) The formation of chlorine by the action of manganese dioxide and sulphuric acid can be used in the absence of bromide and iodide.

Relevant information for the halides: effect of concentrated sulphuric acid.

If there is no residue from the nitric acid treatment, then these anions are absent, and it is necessary to test for the following only: persulphate, nitrite, hypophosphite, formate, acetate, cyanate.

If the silver precipitate was dark coloured it may have been due to one of three things:

(*a*) reduction to metallic silver by a formate (slow in the cold) or a hypophosphite:

(*b*) oxidation to silver peroxide by a persulphate if the solution has a trace of alkalinity:

(*c*) silver sulphide due to thiosulphate which has escaped precipitation by the barium nitrate.

The reducing agents and persulphate will not be there simultaneously. Nitrites may have been destroyed by earlier treatment along with the anions of other easily decomposed acids. In any case the nitric acid solution of the silver precipitate will retain only the acetate ion, if present, of this group, as the others will have reacted either with the silver nitrate or with the nitric acid. The solution should be kept for some of the confirmatory tests below.

PERSULPHATE will only be present if the original substance was soluble in water and has not been treated with sodium carbonate and nitric acid. *Relevant information*: effect of heat; formation of ozone with dilute acids; general oxidizing action.

NITRITE. Nitrous fumes will probably appear when the silver precipitate is dissolved in acid, if nitrites have not already been destroyed. A confirmatory test is the formation of the 'brown-ring' compound with fresh ferrous sulphate solution and acetic acid on the anion solution. *Relevant information*: effect of dilute HCl.

HYPOPHOSPHITE. The formation of metallic silver by reduction of silver nitrate by hypophosphites is accompanied by the formation of silver phosphate which is subsequently dissolved by the nitric acid. The nitric acid solution may therefore be tested with ammonium molybdate (**Phosphates 4**). The other phosphorus acids will have been precipitated as insoluble barium salts. *Relevant information*: effect of heat (PH_3); reduction of concentrated H_2SO_4.

FORMATE. Silver formate is not easily precipitated, but a rapid darkening of the silver nitrate solution on warming will probably be due to a formate. It is difficult to identify a formate in the presence of other carbon acids except by its more vigorous reducing action. In the absence of acetates, thiocyanates, or complex cyanides, ferric chloride gives a characteristic red colour with a neutral solution of a formate, and a basic salt is precipitated on boiling this solution. *Relevant information*: effect of concentrated H_2SO_4.

ACETATE. Silver acetate is moderately soluble and may not appear as a precipitate if the solution is dilute. The liberation of acetic acid vapour, or better, the formation of ethyl acetate by warming with a little alcohol and sulphuric acid, is a good confirmatory test. In the absence of formate, thiocyanate, or complex cyanide, the red colour of ferric acetate is seen on adding ferric chloride to a neutral solution of an acetate, e.g. the anion solution, followed by precipitation of basic ferric acetate on warming.

CYANATE. The decomposition of silver cyanate by nitric acid with evolution of carbon dioxide and formation of ammonium nitrate is characteristic of this ion. Cyanates are the only substances apart from carbonates which give carbon dioxide when treated with dilute acids, and though they are not common, the possibility of their presence should not be overlooked, especially if cyanides are also present. If the anion solution is free from ammonium ion, the presence of this in the nitric acid solution of the silver precipitate is a confirmatory test for cyanates.

Group E: the soluble silver salts

Apart from the sulphate, fluoride, and fluosilicate which will have been precipitated by calcium or barium nitrate, and the sparingly soluble formate, acetate, and nitrite discussed in the last group, the only anions which give no precipitate with silver nitrate are the chlorate, perchlorate, nitrate, and permanganate ions. The filtrate from the silver precipitate may contain these and should be tested as follows.

CHLORATE. Acidify a portion of the filtrate with dilute nitric acid and add granulated zinc. A cloudy precipitate of silver chloride will develop due to the silver ion present as the chlorate is reduced. This will clear again owing to displacement of the silver by the zinc (**Halides 7**), but if the clear solution is decanted it will give a precipitate with silver nitrate. Chlorate may be present as a decomposition product of hypochlorite. *Relevant information*: effect of heat, warm HCl, or concentrated H_2SO_4; deflagration with charcoal.

PERCHLORATE. The detection of a perchlorate in the presence of a chlorate is a difficult matter, as the *quantitative* reduction of the chlorate must first be carried out, and the perchlorate then converted to chloride with, say, titanous sulphate. This and other suitable reducing agents are not often to hand and are rarely chloride-free. It is probably simpler to evaporate the solution of perchlorate (free from chlorate) and ignite to effect the conversion to chloride. *Relevant information*: effect of heat; deflagration with charcoal.

PERMANGANATE. The purple colour of the solution will show the presence of a permanganate, which can be confirmed by reduction in alkaline solution to the green manganate ion and subsequent decolorization in acid solution. *Relevant information*: effect of heat; deflagration on charcoal; effect of concentrated H_2SO_4. Reduction with liberation of sulphur during H_2S precipitations and subsequent detection of manganese during cation analysis.

NITRATE. Tests for the presence of nitrate will have been made before making up the bulk of the anion solution. *Relevant information*: effect of heat and of concentrated H_2SO_4; deflagration with charcoal.

OXIDES. It is practically impossible as a rule to detect free normal oxides of the metals except after quantitative analysis of a substance, although a separation of soluble salts from insoluble oxides is sometimes possible in special cases.

When the elements and radicals present in a substance have been identified, an attempt should be made to deduce so far as is possible from the information available the nature of their association in the substance, and to what extent they are present. In particular a distinction must be made between main constituents and traces.

APPENDIX

Table I

Principal insoluble chlorides

Periodic Group:

IB	IIB	IIIB	IVB	VB
$CuCl$				
$\mathbf{AgCl}$				$SbOCl$
$AuCl$	$\mathbf{Hg_2Cl_2}$	$TlCl$	$\mathbf{PbCl_2}$	$BiOCl$

These are all chlorides of elements in low valency states. Insoluble chlorides of trivalent Nb, Cr, Mo, Rh, Ir, and a few other solid chlorides which are undoubtedly complex in structure can be formed, but not by precipitation methods.

Table II

Insoluble sulphides which can be formed by direct precipitation with hydrogen sulphide

Those in italics are soluble in 0·25 *N* acid and belong to the Second Main Group; the remainder belong to the First Main Group.

Periodic Group:

VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB
	$\boldsymbol{\mathit{MnS}}$	$\boldsymbol{\mathit{FeS}}$	$\boldsymbol{\mathit{CoS}}$	$\boldsymbol{\mathit{NiS}}$	Cu_2S	$\boldsymbol{\mathit{ZnS}}$	$\mathit{Ga_2S_3}$	GeS	$\mathbf{As_2S_3}$	
		$\boldsymbol{\mathit{Fe_2S_3}}$			$\mathbf{CuS}$			GeS_2		
Mo_2S_5		Ru_2S_3	Rh_2S_3	PdS	Ag_2S	$\mathbf{CdS}$	$\mathit{In_2S_3}$	$\mathbf{SnS}$	$\mathbf{Sb_2S_3}$	TeS_2
MoS_3								$\mathbf{SnS_2}$	Sb_2S_5	
$\mathit{UO_2S}$		OsS_2	Ir_2S_3	PtS_2	Au_2S	$\mathbf{HgS}$	$\mathit{Tl_2S}$	$\mathbf{PbS}$	$\mathbf{Bi_2S_3}$	PoS_2(?)
		OsS_4			AuS					

NiS and CoS have forms insoluble in 0·25 *N* acid.

V_2S_5, MoS_3, WS_3, As_2S_5, Sb_2S_5, and possibly Au_2S_3 can be precipitated by acidifying the corresponding alkali thiosalts (thiovanadates, &c.).

GeS_2 is soluble in alkali and in dilute acid. It can be precipitated from 6 *N* acid solution.

TABLE II A

The First Main Group

PERIODIC GROUP:

VI A	VII A	VIII			I B	II B	III B	IV B	V B	VI B
					Cu_2S			GeS	$\mathbf{As_2S_3}$	
					$\mathbf{CuS}$			GeS_2*	As_2S_5*	
Mo_2S_5		Ru_2S_3	Rh_2S_3	PdS	Ag_2S	$\mathbf{CdS}$		$\mathbf{SnS}$	$\mathbf{Sb_2S_3}$	TeS_2
MoS_3*								$\mathbf{SnS_2}$	Sb_2S_5*	
(WS_3)*		OsS_2	Ir_2S_3	PtS_2	Au_2S	$\mathbf{HgS}$		$\mathbf{PbS}$	$\mathbf{Bi_2S_3}$	PoS_2(?)
		OsS_4			AuS					

* See notes on Table II.

TABLE III

The metals in this table are those whose sulphides are soluble in or hydrolysed by water

Those in italics are not precipitated as hydroxides by ammonium hydroxide in the presence of ammonium chloride and constitute the Third Main Group. The remainder belong to the Second Main Group.

PERIODIC GROUP:

I A	II A	III A	IV A	V A	VI A
Li	Be				
Na	*Mg*	Al			
K	*Ca*	Sc	Ti	$(V^{\cdots})$	**Cr**
Rb	*Sr*	Yt	Zr	Nb	
Cs	*Ba*	R.E.'s	Hf	Ta	
—	*Ra*	Ac	Th	Pa	

Except in the case of chromium and vanadium, where the trivalent ion is the one referred to, only the highest states of oxidation have been considered. The variable valency of elements in Groups IV A, V A, &c., the reducing action of H_2S on vanadates, chromates, permanganates, &c., and the unstable or complex nature of the compounds of low valency would make a complete statement unnecessarily complicated.

TABLE III A

The Second Main Group

PERIODIC GROUP:

IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB
Be											
	Al										
	Sc	Ti	(V)*	**Cr**	***Mn***	***Fe***	***Co***	***Ni***		***Zn***	*Ga*
	Yt	Zr	Nb								*In*
	R.E.'s	Hf	Ta								*Tl*
	Ac	Th	Pa	*UO_2S*							

The sulphides of those in italics are not hydrolysed in water.

Vanadium in its highest state of oxidation (as vanadate) behaves in a manner rather similar to that of the phosphate radical in Group V B. For comments on the other 'rare' elements see Tables II and III.

TABLE IV

The distribution of the soluble and insoluble barium salts

PERIODIC GROUP:

III	IV	V	VI	VII	VIII
H_3BO_3	HCN	HNO_2	H_2O	**H_2F_2**	
	HCNO	HNO_3	H_2O_2		
	HCNS				
	H.COOH				
	CH_3.COOH				
	H_2CO_3				
	$(COOH)_2$				
	$(CH.OH.COOH)_2$				
	H_2SiO_3	$H(H_2PO_2)$	H_2S	HCl	
		$H_2(HPO_3)$	**H_2SO_3**	HClO	
		HPO_3	**$H_2S_2O_3$**	$HClO_3$	
		$H_4P_2O_7$	**H_2SO_4, H_2CrO_4**	$HClO_4$, $HMnO_4$	$H_4Fe(CN)_6$
		H_3PO_4	$H_2S_2O_8$		$H_3Fe(CN)_6$
		H_3AsO_3		HBr	
		H_3AsO_4		**$HBrO_3$**	
				HI	
				HIO_3	

Acids forming soluble or hydrolysed barium salts are printed in ordinary type. Acids forming insoluble barium salts are printed in black type.

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chem. = chemistry and reactions.
s.s. = identification in single substance.
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